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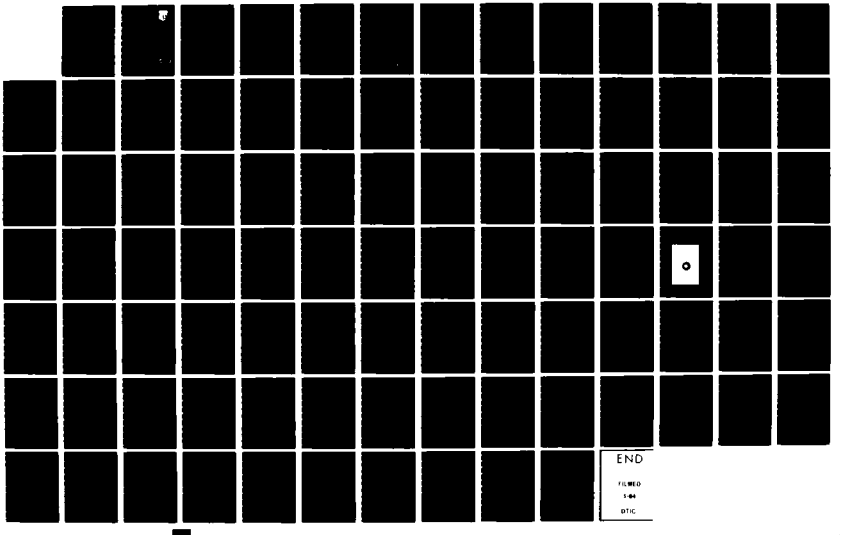

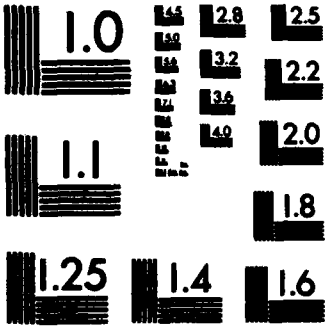

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MODEL COMPOUND STUDIES OF RIGID ROD AROMATIC HETEROCYCLIC POLYMER SYSTEMS, THE X-RAY CRYSTAL STRUCTURE OF 2,6-DIPHENYLBENZO (1,2-d; 5,4-d') DIIMIDAZOLE TETRAHYDRATE, $C_{20}H_{14}N_4 \cdot 4H_2O$, A MODEL SYSTEM FOR THE STUDY OF POLYMER-WATER INTERACTION IN POLYBENZIMIDAZOLES

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July 1983

Final Report for Period 1 August 1981 - 30 September 1982.

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This technical report has been reviewed and is approved for publication.

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FOR THE COMMANDER

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model compound	x-ray diffraction

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The crystal and molecular structure of 2,6-diphenylbenzo (1,2-d;5,4-d') diimidazole tetrahydrate, $C_{20}H_{14}N_4 \cdot 4H_2O$, is determined by single crystal x-ray diffraction. The benzodiimidazole compound is used as a model compound for poly(p-phenylenebenzodiimidazole), a rigid rod polymer.

The crystals grown from ethanol are well formed, translucent, and amber tinted. The space group is $P2_1/c$ (monoclinic), with cell constants $\underline{a}$ = 9.008(2)Å, $\underline{b}$ = 24.967(7)Å, $\underline{c}$ = 9.870(5)Å, β = 119.82(3)°. There are four molecules per unit

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20. Abstract

cell of volume 1925.8(1.3)$\AA^3$, and the measured density is 1.295 g/cc.

4850 unique reflections out to 56° in 2θ were collected with an automated diffractometer using niobium filtered MoK$_\alpha$ radiation. The 2θ scan technique was employed. Absorption corrections were made and approximately 11,000 reflections were averaged to give a hemisphere of independent observations. The direct method of phase determination was used to solve the structure, and full matrix least squares refinement gave a final R_w factor of 0.084 based on the 3570 reflections with $F_{obs} \geq 3\sigma(F)$.

The central benzodiimidazole portion of the molecule is essentially planar, while the end phenyl rings are twisted in the same direction from the central plane by 6.0° and 7.9°. The carbon-nitrogen bonds on the imidazole rings are semi-localized, and the one lone electron pair nitrogen atom on each ring is positioned cis to that on the other ring. Molecules pack in herringbone fashion, held in the crystalline lattice by the strong hydrogen bonding provided by a three dimensional water structure. Four hydrogen bonded water molecules bridge the two lone electron pair nitrogen atoms on each molecule to form a ring. Each water molecule participates in hydrogen bonding with other molecules related by symmetry centers along the a and c axes so that two water molecules make use of all four possible coordination sites, while the other two make use of three. D-spacings in the polymer film are correlated with d-spacings of selected intense reflections in the single crystal. Powder diffraction patterns of the model compound are recorded for comparison with computer generated patterns and polymer film data. Implications of the model compound structure to the problem of water retention in polymer synthesis and processing are presented.

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division, and The University of Dayton Research Institute under contract F33615-81-C-5019 to the Materials Laboratory. The work was initiated under Project No. 2303, "Research to Define the Structure Property Relationships," Task No. 2303Q3 Work Unit Directive 2303Q307, "Structural Resins." Dr. Thaddeus E. Helminiak served as the AFWAL/ML Work Unit Scientist. Co-authors were Marilyn Hunsaker and W. W. Adams, Materials Laboratory (AFWAL/MLBP); and Dr. Albert V. Fratini, University of Dayton Research Institute.

This report covers research conducted from August 1981 to September 1982.

The authors express their appreciation to Douglas S. Dudis, who as an undergraduate student at the University of Dayton first prepared crystals of the model compound and recorded the initial x-ray photographs. Thanks are due to Mary Ryan for NMR Spectra and to Gary Griffin of the University of Dayton Research Institute for assistance in adapting computer programs to the PRIME 550. Thermogravimetric/mass spectral analysis and differential scanning calorimetry measurements were performed by E. G. Jones of Systems Research Laboratories and E. Soloski of the University of Dayton Research Institute.

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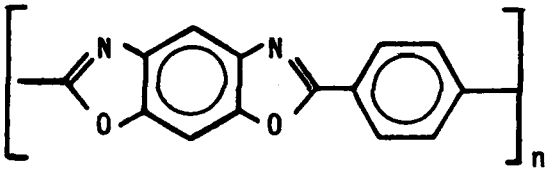
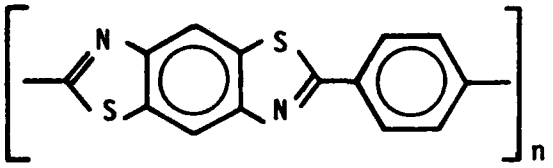
SECTION I

BACKGROUND

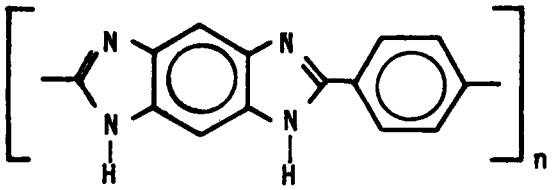
Polymers are useful as structural materials due to their high strength-to-weight ratio, ease of processing, and availability of structural variations to control both mechanical and physical properties. In response to the need for high temperature adhesives and coatings, heat resistant fibers, and ablative systems, polymer scientists have been active in research in the area of thermally stable polymers for more than 20 years. Recently, particular emphasis has been placed on high temperature resistant, rodlike, aromatic heterocyclic polymers shown below. The para-configured poly (p-phenylenebenzobisoxazole) (PBO) and poly (p-phenylenebenzobisthiazole) (PBT), in particular, demonstrate high tensile strength, high modulus and good thermooxidative stability when solutions are spun into films and fibers (Reference 1).



PBO



PBT



PDIAB

As a class of polymers, the polybenzimidazoles are notable as heat-resistant polymers. Thermogravimetric analysis of wholly aromatic polybenzimidazoles showed weight losses starting around 600°C, reaching about 30% at 900°C (Reference 2). Unfortunately, these wholly aromatic polybenzimidazoles exhibit a high affinity for water, making these materials less attractive as structural materials when compared to the polybenzoxazoles and polybenzothiazoles. In (p-phenylenebenzodiimidazo)

polymer (PDIAB), the attraction for water is so pronounced that continued heating under vacuum does not completely eliminate the water. The nature of the polymer-water interaction in PDIAB is discussed more fully in Section V.

Polymer thermal stability is primarily dependent on the bond energy between atoms in a molecule. The strength of the chemical bond represents the upper limit of vibrational energy that the molecule may possess before bond dissociation occurs (about 100 kcal/mol for a single covalent bond). Intramolecular bond strength may be enhanced by resonance stabilization. The incorporation of aromatic or heterocyclic rings in the molecule may contribute 40 to 70 kcal/mol to the energy. Intermolecular attraction between neighboring atoms can add additional thermal stability. These interactions include van der Waals forces (about 0.5 kcal/mol, dipole-dipole interactions (about 6 kcal/mol), and hydrogen bonding (about 10 kcal/mol) (Reference 3).

The definition of thermal stability varies with the time and temperature requirements of the intended use. For example, Cassidy's definition of thermal stability (Reference 4) is the retention of physical properties at 250^{o}C for extended periods; at 500^{o}C for intermediate periods; and at 1000^{o}C for short periods. A polymer may fail to reach the latter criteria and yet be satisfactory for the thermal requirements of its application.

Degree of crystallinity can influence thermal stability. Historically, polymer chemists sought to maximize the crystallinity of the system by designing molecules with a high degree of structural regularity, streamlined for optimum packing and exhibiting strong inter-chain bonding. Early in the 1960's, thermal stability to temperatures as high as 400-600^{o}C in air by thermogravimetric analysis was realized for polyamides, polyimides, and polyoxazoles (Reference 3). Although stability up to 800^{o}C in nitrogen was observed for polyquinoxalines and polyphenylenes, most high temperature polymers synthesized in the ensuing years had thermal stabilities in the 350-550^{o} range.

Once polymer chemists felt that the upper limit of high temperature stability had been reached, attention turned to the problem of tractability.

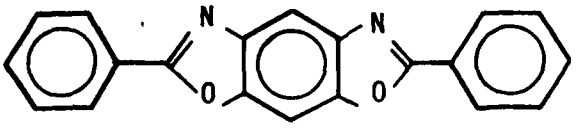
The problem of thermal stability versus tractability is exemplified in a class of materials known as semi-ladder polymers. These aromatic heterocyclic systems derive their thermal stability from the extension and stiffness of the chain. But structural characteristics which give these materials their superior thermal and mechanical properties also make them difficult to process (Reference 5). Strong mineral or organic acids are required as solvents, and the polymer morphology can be influenced only to a limited extent after processing.

The difficulty in processing these polymers led to the concept of using blends of paraconfigured and metaconfigured semi-ladder polymers. The flexibility in the backbone of the metaconfigured semi-ladder polymers would enhance ductility in the blend in the solid state. Reinforcing the flexible polymer with a rod-like polymer results in composites analogous to chopped fiber reinforced composites, combining the thermal stability of both polymers with the flexibility of the coil polymer. Various molecular composites have been studied recently for their mechanical and morphological properties as well as their tractability (Reference 6). In several of these blends reported to date, PDIAB functions as the reinforcing component.

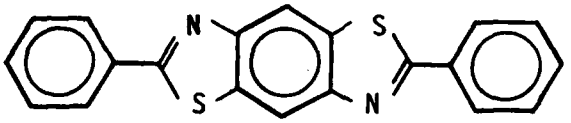
Ideally, a molecular composite should be a homogeneous dispersion of rod polymers in the coil matrix. Electron microscopy can provide some information concerning the extent of dispersion, but for information on the atomic scale of the blends, x-ray or electron diffraction studies are required. Wide angle x-ray scattering patterns can reveal the orientation distributions as well as crystallite size and inter- and intra-molecular plane spacings. X-ray studies on the polymers are greatly facilitated by structure determination of model compounds (References 7 through 11). Detailed structure information on the individual polymer blend components can be extrapolated from the molecular geometry of the model compound.

For example, recent interpretation of diffraction patterns of PBO and PBT have relied heavily on the detailed structure analysis of the

model compounds 2,6-diphenylbenzo-(1,2-d; 5,4-d')bisoxazole (c-bisoxazole) and 2,6-diphenylbenzo-(1,2-d; 4,5-d')bisthiazole (t-bisthiazole) (References 7 through 11). The diffraction



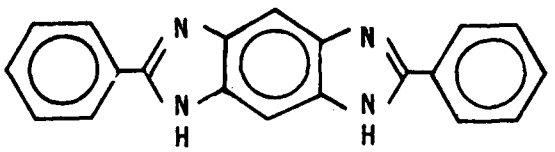
c-bisoxazole



t-bisthiazole

patterns of fibers of PBT exhibit strong Bragg-equatorial reflections at 3.4 and 5.9Å, and many meridional layer lines with a fiber repeat distance of 12.41 (3)Å. These spacings have been interpreted, based upon comparison to the model compound crystal structures, as the lateral separation of adjacent molecules, packed as highly oriented rods of high chemical perfection.

This report presents the crystal structure analysis of 2,6-diphenylbenzo (1,2-d; 5,4-d') diimidazole, hereafter referred to as the diimidazole model compound, a model compound for the rigid rod poly (1,7-dihydrobenzo [1,2-d: 4,5-d'] diimidazole - 2,6-diyl-1,4-phenylene) (PDIAB).



diimidazole model compound

This structure serves to provide not only accurate molecular parameters for the monomer repeat unit for use in subsequent structural analysis of PDIAB fibers and blends, but also a glimpse into the nature of the polymer-water interaction in polybenzimidazoles.

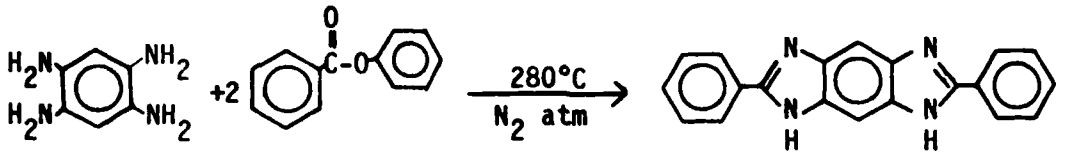
Powder diffraction patterns have been recorded for the diimidazole model compound. The patterns of the ethanol grown and sublimed crystals are checked for structural similarities and compared with the computer generated pattern.

SECTION II

EXPERIMENTAL

1. SYNTHESIS

The diimidazole model compound was prepared in crude form by Dr. Fred Arnold, Polymer Branch, Materials Laboratory. The synthesis followed the original procedure of Vogel and Marvel (Reference 12), in which the stoichiometric combination of tetraamine and phenyl benzoate in melt condensation gave the desired product:



The product, 2,6-diphenylbenzo (1,2-d;4,5-d') diimidazole tetrahydrate, had a chemical formula of $C_{20}H_{14}N_4 \cdot 4H_2O$ and a molecular weight of 382.20 g/mol.

The proton nmr spectrum of the product in the nonprotonating solvent N,N'-dimethylacetamide (DMAC) has revealed the presence of two OH peaks at δ = 3.6 and 8.0. All chemical shifts are relative to TMS. There are also two additional solvent NCH_3 peaks which are shifted upfield by 6 Hz from their position in the neat solvent, indicating the formation of one or more complexes between the model compound, water and DMAC.

Crystals suitable for diffraction studies were obtained both by vacuum sublimation at 360°C and by slow evaporation from ethanol.

2. CRYSTAL MORPHOLOGY

The ethanol-grown crystals were well formed parallelepipeds with an ambient tint, while sublimation provided clusters of single crystals similar in morphology to the ethanol-grown crystals though smaller in size.

The ethanol-grown crystals were superior to the sublimed crystals in terms of diffraction characteristics. While polybenzimidazoles are known to be hygroscopic (Reference 13), microscopic inspection of the crystals after standing for several months at room temperature and humidity showed no deterioration apparently because the equilibrium water content was satisfied during crystal growth.

A translucent amber needle grown from ethanol was glued (Eastman 910 adhesive) onto a glass fiber with the needle parallel to the fiber direction. The fiber was mounted on the goniometer head with hard wax and visually oriented with the aid of a microscope. A second crystal, chipped from a large cluster, was mounted perpendicular to the wide face and used solely for precession and Weissenberg photography.

Another crystal, chosen from the batch of sublimed crystals was mounted in a similar manner and crystal structure analysis was attempted to examine possible retained solvent effects. This crystal, though beautifully formed, scattered weakly and as a result was unsuitable for an accurate crystallographic structure determination.

3. SPACE GROUP AND CELL CONSTANTS

The precession photographs of ethanol-grown crystals indicated the monoclinic space group $P2_1/c$(C_{2h}^5, No. 14 in the International Tables for X-ray Crystallography, Vol. 1) (Reference 14). Even though the alternate space group, $P2_1/n$, actually corresponded to the reduced cell, we decided to proceed with the non-reduced $P2_1/c$ cell since it is the more conventional setting in the International Tables, Volume I. The transformation from the $P2_1/c$ to the reduced $P2_1/n$ cell is:

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 1 & 0 & 1 \end{bmatrix} \begin{bmatrix} h \\ k \\ \ell \end{bmatrix} = [h' \; k' \; \ell']$$

where $hk\ell$ are the Miller Indices for the $P2_1/c$ cell and $h'k'\ell'$, those of the $P2_1/n$ cell.

Accurate cell parameters were determined for ethanol-grown crystals by centering 14 reflections and their Friedel mates ($35^{o} < 2\theta < 38^{o}$) on the diffractometer using molybdenum Kα radiation (λ = 0.7107 Å), followed by two cycles of least squares refinement (Table 1).

Precession photography on the sublimed crystal also revealed the same $P2_1/c$ space group. The cell parameters were determined in the same manner as the ethanol grown crystal; only 8 reflections and their Friedel mates were centered ($18^{o} < 2\theta < 24^{o}$).

4. DENSITY

Density measurements were made by the flotation in aqueous cesium chloride. A sample of the solution was then weighed in a pycnometer to determine the density at room temperature.

A density of 1.07 g/cc was calculated on the basis of four molecules per unit cell. A measured density of 1.295 g/cc for the ethanol grown crystal was the first indication that solvent had been incorporated into the structure. This seemed reasonable, given the characteristic absorption of water by benzimidazoles as previously mentioned.

Determination of the structure confirmed the presence of 16 water molecules per unit cell, corresponding to a calculated density of 1.319 g/cc. It is interesting to note that the sublimed material had a similar measured density of 1.304 g/cc suggesting that water was carried along in the sublimation process.

TABLE 1

SUMMARY OF CRYSTAL DATA FOR DIIMIDAZOLE MODEL COMPOUND

	Ethanol-Grown Crystals	Sublimed Crystals+
a	9.008(2)Å	9.02(2)Å
b	24.967(7)Å	24.97(3)Å
c	9.870(5)Å	10.02(3)Å
α	90.0°	90.0°
β	119.82(3)°	119.12(4)°
γ	90.0°	90.0°
Volume of unit cell	1925.8(1.3)Å3	1960Å3
Measured density	1.295 g/cc	1.304 g/cc
Calculated density	1.319 g/cc	1.296 g/cc
F (0, 0, 0)	808	808
Linear absorption coefficient for MoKα radiation	0.877 cm^{-1}	0.877 cm^{-1}
Z	4	4
Water molecules per unit cell	16	16
Space group	$P2_1/C$	$P2_1/C$
Crystal system	Monoclinic	Monoclinic
Absorption factor min=	0.9883	
max=	0.9922	
ave=	0.9907	
Crystal volume	0.085 mm^3	< 0.08 mm^3

+A complete x-ray analysis was not performed on these crystals due to the lack of data at high 2θ angles. Note the similarity in cell dimensions between the ethanol-grown and sublimed crystals indicating nearly equivalent structures.

SECTION III

DATA COLLECTION

1. DESCRIPTION OF THE INSTRUMENT

X-ray intensity data were collected on a computer-controlled Picker FACS-I diffractometer equipped with pulse height analyzer and NaI scintillation detector. Each reflection was recorded and stored on magnetic tape. The control programs used were written by Dr. P. Galen Lenhert of Vanderbilt University (Reference 15).

A standard focus molybdenum tube, operated at 50 kV (constant potential) and 12 mA, was used as the x-ray source for data collection. The $K\beta$ radiation was reduced by an incident beam niobium filter 0.005" in thickness. A symmetrically variable aperture (SVA) was placed near the counter (3.75 mm^2).

For data collection, the incident and diffracted beams were collimated by hollow cylinders tapered to 1.0 mm in diameter, approximately 23.5 cm from the crystal. The incident beam collimator was designed to hold the niobium filter, and the diffracted beam collimator contained independent pairs of top-bottom, left-right slit adjustments for use in crystal orientation. A calibrated microscope, attached at an angle to the chi circle, was used to center the crystal precisely. The optical centering was confirmed by comparison of positive and negative 2θ values for several reflections. The microscope was also calibrated for measurements of crystal size used later for absorption corrections.

2. DATA COLLECTION

The crystal was mounted on the diffractometer with the a axis coincident with ϕ. A stereoplot of the crystal morphology is shown in Figure 1. A total of 11,431 reflections were measured for the ethanol-grown crystal, using a θ-2θ scan mode. Four equivalent octants of the sphere of reflection were measured ($hk\ell$, $\bar{h}k\ell$, $h\bar{k}\ell$, $\bar{h}\bar{k}\ell$). Intensities were recorded with a scan speed of 1^o per minute for reflections of $2\theta < 56^o$. Scattering background counts were measured at equal angles above and below the respective values of the $K\alpha_1$ peaks. Each background was

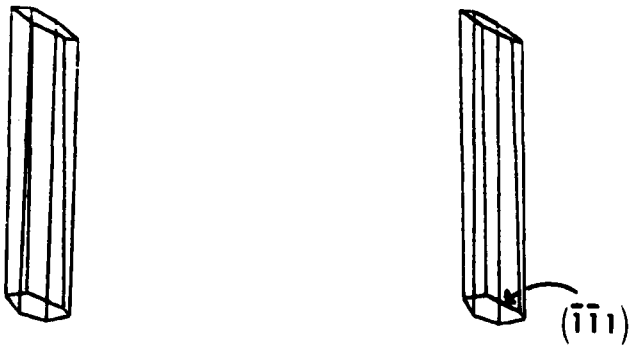


Figure 1. A Stereoplot of the Data Crystal Grown from Ethanol. Prominent side faces starting with the broad rear face and moving in a clockwise direction around the crystal are (1̄11), (32̄3), (010), (121̄), (3̄2̄3̄), and (01̄0). The slanted top face is (100). The crystal was mounted with the vertical needle axis parallel to ϕ.

counted for about half the total peak scan time so that the scan time and total background times were approximately equal. Three standard reflections were recorded every 96 reflections with little observable decrease in intensity during the two months of data collection. In addition, four extra standards were checked periodically to monitor instrument stability. Table 2 contains summary of data collection.

3. DATA REDUCTION

Raw intensity data consisted of a scan count (C) and scan time (t_c), two background counts (b_1 and b_2) taken for a total time, t_b, on either side of the peak. Raw intensities were first processed to obtain the observed intensity (I_{obs}):

$$I_{obs} = C - \frac{(b_1 + b_2)t_c}{t_b}$$

The standard deviation, based on counting statistics alone, was:

$$\sigma(I_{obs}) = \left[C + (b_1 + b_2)\left(\frac{t_c}{t_b}\right)^2\right]^{1/2}$$

TABLE 2

SUMMARY OF DATA COLLECTION

2θ range	0-56°
Reflection base width	1.3°
Dispersion factor	0.346°
No. of background counts per reflection	2
No. of peak scan per reflection	1
Background time per reflection	approximately twice the scan time
Scan speed	1°/min
Attenuation filter factors	2.163 for reflections 141, 151, 111 and 120
	1.000 for all other reflections
Balanced filters	none
Take off angle	2.0°
Symmetrical variable aperture (SVA) dimensions	3.75 x 3.75 mm
Radiation for data collection	MoKα (Nb-filtered)

The data were collected in scale groups separated by successive measurements of standard reflections. Long term x-ray fluctuations were corrected by scaling each group to the current measurement of the standard intensities compared to the current average of standard intensities measured to that time:

$$K = \frac{k}{\Sigma I_{std}}$$

The arbitrary constant k was set equal to 200,000 for this determination.

The conventional Lorentz (L) and polarization (p) factors were applied and corrections for absorption of the beam by the crystal were calculated using crystal orientation, size and shape measured as described previously.

The value of 0.877 cm^{-1} for μ was calculated with the MURHO Fortran program of Lenhert (Reference 16) using the mass absorption coefficients tabulated in International Tables, Vol. III (Reference 14). The x-ray path distance was calculated for each reflection by considering crystal boundaries shown in Figure 1 and crystal orientation with respect to the incident beam. The absorption integral was numerically evaluated over the volume of the crystal for each reflection with the ORABS Fortran program of Wehe, Busing and Levy (Reference 17). Values of the transmission factor (A) ranged from 0.9883 to 0.9922, with an average of 0.9907.

These corrections were applied to the observed intensity to give the experimental magnitude of the structure factor:

$$|F_{obs}|^2 = \frac{I_{obs} K}{LpA}$$

The standard deviation of F^2 based on counting statistics alone was

$$\sigma(F_{obs}) = \frac{\sigma(I_{obs}) K}{LpA}$$

and the variance of F^2 was

$$\sigma^2(|F_{obs}|)^2 = \frac{\sigma^2(I_{obs}) K^2}{L^2 p^2 A^2}$$

Data reduction was accomplished using the ORABS Fortran program (Reference 17). Input for data reduction included raw intensity data with data collection conditions specified, a list of attenuation filter factors, crystal shape data and linear absorption coefficient, and unit cell parameters. Before actual structure determination was begun, equivalent and multiply measured reflections were sorted and averaged.

SECTION IV

STRUCTURE DETERMINATION

The structure was solved by application of the Fortran program MULTAN 80 (Reference 18), which assigned the phases of 296 reflections with normalized structure factors (E's) $\geq$ 1.9 from a starting set comprised of three origin-defining reflections [129, 0; 215, 0; 727, π], where 0 refers to a positive phase and π refers to a negative phase, and four additional reflections [4 24 $\bar{4}$, 0; 2 5 0, π; 8 3 $\bar{3}$, 0; 2 15 $\bar{6}$, 0]. The corresponding E-map gave plausible positions for 24 non-hydrogen atoms in the structure.

The four solvent molecules, later shown to be water molecules, were located in a difference Fourier map, which followed two cycles of isotropic least squares refinement carried out by CRYLSQ, a subroutine of the Fortran program XRAY 72 (Reference 19).

Subsequent difference Fourier syntheses located all 14 hydrogen atoms of the benzodiimidazole molecule and 7 of the 8 hydrogen atoms associated with the water structure. A thermal ellipsoid plot of the molecule, including the numbering system, is shown in Figure 2.

Refinement of the water structure was carried out by an iterative process in which atomic positions were adjusted slightly according to the location of positive or negative electron density ("peaks" or "holes") in the difference map. In the case of O4 and its bonded hydrogen atoms, H07 and H08, residual peaks and holes remained near these hydrogen atoms. When the two hydrogen atoms were removed and a difference Fourier map was recalculated, a smeared region of electron density resulted. A representative difference density map of this region is included in Figure 3. H08 could not be accurately pinpointed, which indicates some disorder in the water structure, and was omitted from the final cycles of refinement.

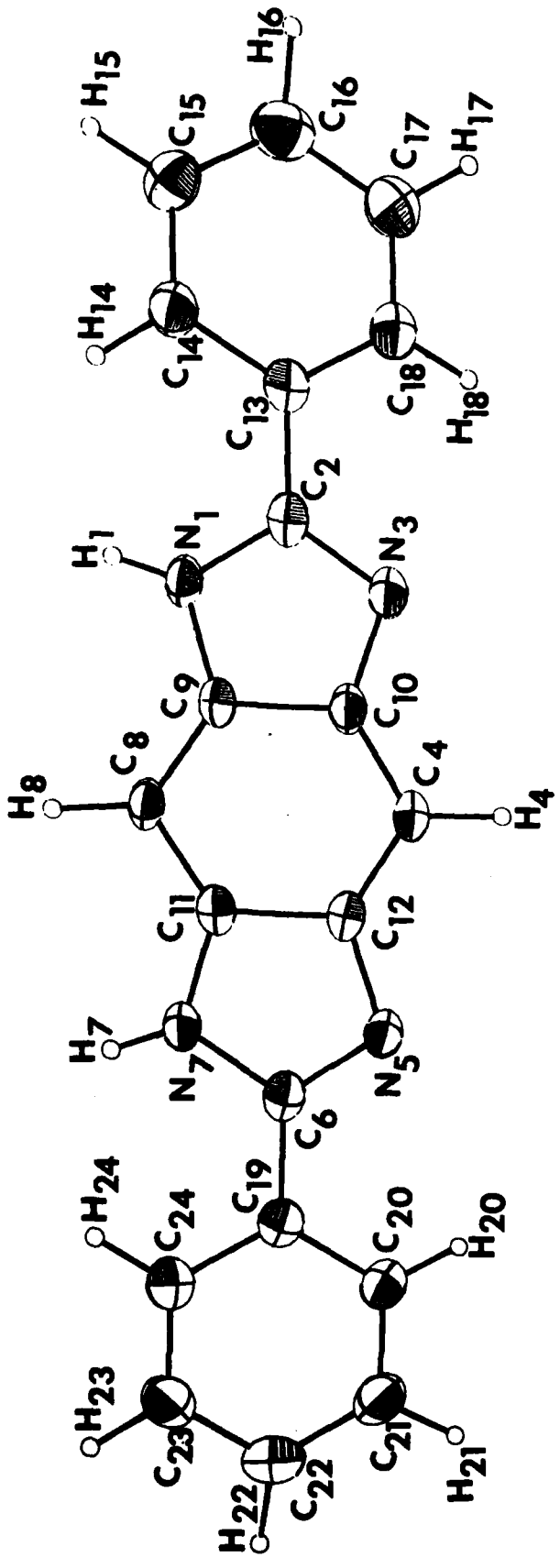


Figure 2. Thermal Ellipsoid Plot of the Diimidazole Model Compound Showing the Numbering System.

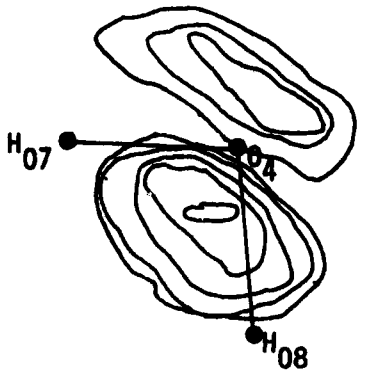


Figure 3. Residual Difference Density in the Vicinity of Water Molecule 4. Atoms H08 and H07 are included in the Map. Contours are at intervals of 5×10^{-2} e/Å^3. The lowest contour is at 30×10^{-2} e/Å^3.

For the final refinement of all 49 atoms in the asymmetric unit, anisotropic temperature factors were used for all non-hydrogen atoms, expressed in the general form:

$$T = \exp\left[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^* + 2U_{12}hka^*b^* + 2U_{13}h\ell a^*c^* + 2U_{23}k\ell b^*c^*)\right]$$

where a^*, b^* and c^* are the reciprocal cell constants, and Uij, the components of a symmetric matrix describing the orientation and three major axes of an equiprobability ellipsoid of thermal vibration.

An additional variable, S, was included to place the observed structure factors $|F_o|$ and the calculated structure factors $|F_c|$ on a common scale. The parameters were varied to minimize the function

$$L = \sum_{hk\ell} w(hk\ell)\left(|F_o(hk\ell)| - S|F_c(hk\ell)|\right)^2$$

where the reliability of each term in the sum was weighted by a factor $w(hk\ell)$, estimated as $w(hk\ell) = 1/\sigma^2 \; |F_o(hk\ell)|$ and calculated from counting statistics as described by Miller, Joesten and Lenhert (Reference 20). The final refinement used only F's $\geq 3\sigma$.

The final residual index for all measured reflections $R_w = (\Sigma w| \; |F_o| - |F_c||/\Sigma w|F_o|)$ was 0.084, based on 3570 reflections. The magnitude of $[\Sigma w||F_o| - |F_c||^2/(m - n)]^{1/2}$, where m is the number of reflections and n, the number of parameters defined, was 1.822. The average shift/error was 0.029 and 0.030 for nonhydrogen and hydrogen atom refinements respectively. The maximum shift/error was 0.301 and 0.191. A final difference synthesis showed no peaks above 0.36 eA^{o-3}, with the exception of a peak in the vicinity of the disordered water (O4, H07, and H08), where the electron density was 0.61 eA^{o-3}. Table 3 (see Appendix) lists the observed and calculated structure factors. Tables 4, 5, and 6 list the fractional coordinates for nonhydrogen and hydrogen atoms, with their thermal parameters. Atomic scattering factors for non-hydrogen atoms were those of Cromer and Mann (Reference 21) and for hydrogen atoms, those of Stewart, Davidson, and Simpson (Reference 22). Calculations for MULTAN 80 were performed on the Prime 550; for XRAY 72, on the CDC 6600, both at Wright-Patterson Air Force Base, Ohio.

TABLE 4

FRACTIONAL ATOMIC COORDINATES FOR NON-HYDROGEN ATOMS
WITH STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z
O1	0.17974(25)	0.45513(9)	0.66875(23)
O2	0.19769(32)	0.62610(10)	0.83752(29)
O3	0.14868(27)	0.56144(8)	0.58426(24)
O4	0.52865(32)	0.63848(11)	1.07177(31)
N1	0.35231(30)	0.55994(9)	1.43324(27)
C2	0.48124(39)	0.58762(12)	1.43252(35)
N3	0.51130(31)	0.57032(10)	1.32069(29)
C4	0.36788(40)	0.49772(12)	1.11888(37)
N5	0.18440(33)	0.42266(10)	0.94658(28)
C6	0.05893(40)	0.39541(12)	0.94874(35)
N7	0.02811(31)	0.41293(10)	1.06298(28)
C8	0.16171(39)	0.48492(12)	1.26643(36)
C9	0.29073(35)	0.52239(12)	1.31520(32)
C10	0.39337(37)	0.52935(12)	1.24364(34)
C11	0.24056(36)	0.45995(12)	1.06811(33)
C12	0.14001(35)	0.45405(12)	1.14256(33)
C13	0.57338(40)	0.63083(12)	1.54275(36)
C14	0.54190(43)	0.64287(13)	1.66351(39)
C15	0.62653(48)	0.68443(15)	1.76545(42)
C16	0.74292(51)	0.71466(15)	1.74637(45)
C17	0.77927(52)	0.70245(17)	1.62950(49)
C18	0.69150(48)	0.66129(15)	1.52606(42)
C19	-.04070(39)	0.35251(12)	0.84046(35)
C20	-.02020(42)	0.34051(13)	0.71344(39)
C21	-.11988(46)	0.30166(14)	0.60639(40)
C22	-.23836(45)	0.27288(14)	0.62612(41)
C23	-.25837(46)	0.28423(15)	0.75261(44)
C24	-.15977(44)	0.32325(13)	0.86026(39)

TABLE 5

ANISOTROPIC THERMAL PARAMETERS OF NON-HYDROGEN ATOMS ($\times 10^3$) WITH STANDARD DEVIATIONS IN PARENTHESES. THE THERMAL PARAMETERS ARE OF THE FORM

$$T = \exp\left[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}h\ell a^*c^* + 2U_{23}k\ell b^*c^*)\right]$$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O1	50(1)	64(2)	52(1)	8(1)	33(1)	13(1)
O2	92(2)	87(2)	89(2)	-25(2)	71(2)	-31(2)
O3	60(2)	55(2)	57(1)	- 2(1)	38(1)	1(1)
O4	77(2)	104(2)	98(2)	10(2)	55(2)	15(2)
N1	44(2)	47(2)	47(2)	1(1)	34(1)	- 1(1)
C2	44(2)	45(2)	47(2)	2(2)	31(2)	4(2)
N3	50(2)	51(2)	55(1)	- 8(1)	39(1)	- 8(1)
C4	54(2)	58(2)	57(2)	-10(2)	45(2)	- 7(2)
N5	58(2)	45(2)	50(2)	- 4(1)	40(1)	- 3(1)
C6	48(2)	43(2)	46(2)	7(2)	31(2)	7(2)
N7	47(2)	45(2)	52(2)	- 3(1)	37(1)	- 2(1)
C8	50(2)	44(2)	50(2)	3(2)	39(2)	1(2)
C9	33(2)	43(2)	40(2)	3(1)	24(1)	0(2)
C10	44(2)	47(2)	46(2)	- 1(2)	32(2)	0(2)
C11	43(2)	47(2)	42(2)	2(2)	29(2)	0(2)
C12	37(2)	39(2)	43(2)	2(1)	26(2)	4(2)
C13	48(2)	42(2)	47(2)	2(2)	29(2)	2(2)
C14	54(2)	50(2)	52(2)	0(2)	33(2)	- 2(2)
C15	72(3)	54(2)	58(2)	4(2)	39(2)	- 1(2)
C16	83(3)	57(3)	64(3)	-15(2)	32(2)	-14(2)
C17	91(3)	82(3)	82(3)	-39(3)	57(3)	-20(3)
C18	72(3)	70(3)	67(3)	-20(2)	49(2)	-16(2)
C19	46(2)	39(2)	42(2)	5(2)	24(2)	3(2)
C20	61(2)	52(2)	60(2)	- 3(2)	41(2)	- 5(2)
C21	72(3)	59(2)	58(2)	2(2)	40(2)	- 9(2)
C22	63(3)	49(2)	55(2)	1(2)	22(2)	- 2(2)
C23	65(3)	66(3)	60(2)	-18(2)	35(2)	- 5(2)
C24	69(2)	58(2)	55(2)	-10(2)	40(2)	- 5(2)

TABLE 6

FRACTIONAL HYDROGEN ATOM COORDINATES WITH STANDARD DEVIATIONS IN PARENTHESES AND ISOTROPIC THERMAL PARAMETERS ($x10^2$)

Atom	x	y	z	U
H1	0.3046(30)	0.5647(10)	1.4869(28)	5.0
H4	0.4407(30)	0.5009(9)	1.0750(28)	5.0
H7	-.0487(31)	0.4011(9)	1.0794(28)	5.0
H8	0.0832(30)	0.4803(10)	1.3042(27)	5.0
H14	0.4537(30)	0.6246(9)	1.6705(28)	6.0
H15	0.5989(32)	0.6915(10)	1.8529(29)	6.0
H16	0.8198(30)	0.7415(11)	1.8291(29)	6.0
H17	0.8706(31)	0.7213(10)	1.6221(29)	6.0
H18	0.7190(32)	0.6504(10)	1.4459(30)	6.0
H20	0.0689(31)	0.3565(10)	0.7043(28)	5.0
H21	-.0995(32)	0.2958(10)	0.5211(30)	6.0
H22	-.3448(30)	0.2474(11)	0.5304(29)	6.0
H23	-.3538(31)	0.2677(10)	0.7611(30)	6.0
H24	-.1707(33)	0.3324(10)	0.9532(29)	6.0
HO1	0.3020(35)	0.4414(11)	0.6882(31)	7.0
HO2	0.1987(33)	0.4484(10)	0.7515(31)	6.0
HO3	0.1739(32)	0.6114(10)	0.7647(30)	6.0
HO4	0.3622(30)	0.6234(10)	0.9403(28)	5.0
HO5	0.0250(31)	0.5580(10)	0.4921(29)	5.0
HO6	0.1727(31)	0.5366(10)	0.6256(28)	5.0
HO7	0.5972(34)	0.6274(11)	1.0694(31)	7.0

SECTION V

RESULTS AND DISCUSSION

Determination of the structure reveals a nearly planar diphenyl-benzodiimidazole molecule with semilocalized carbon-nitrogen double bonds. The nitrogen atoms with lone electron pairs are positioned cis to each other. The monomer repeat distance, as measured by the C16-C19 separation, is 12.197(6)Å, which would correspond to the polymer repeat in rodlike PBI. Molecules pack in herringbone fashion, held in the crystalline lattice by a network of solvent water molecules. Features of the structure discussed in this section include:

- Atomic Coordinates, Bond Lengths and Angles
- Least Squares Planes
- The Molecule: Central Benzene Ring, Substituent Phenyls, Imidazole Rings
- Water Structure
- Packing
- Relationship to Polymer Film and Fiber Data
- X-Ray Powder Diffraction Patterns
- Simulated Powder Patterns Computed with POWD7

1. ATOMIC COORDINATES, BOND LENGTHS AND ANGLES

The final fractional coordinates and anisotropic temperature factors for non-hydrogen atoms are listed in Tables 4 and 5. Estimated standard deviations, obtained from the last cycle of least squares refinement, average 0.0002Å for atom coordinates in the central benzodiimidazole moiety. The substituent phenyl groups, exhibiting greater thermal motion, show a slightly higher average standard deviation of 0.0003A in their atomic positions.

Hydrogen atom fractional coordinates and isotropic temperature factors are listed in Table 6. The average standard deviation for hydrogen atoms is 0.002Å, one order of magnitude higher than the average for non-hydrogen atomic positions.

Bond lengths and angles with estimated standard deviations are summarized in Tables 7 and 8. The average standard deviation for distances in the central ring system is 0.004Å, and in the phenyl substituents, 0.006Å. Bond distances to hydrogen atoms as expected, have much higher average standard deviations of 0.03Å.

Bond angles show a similar trend in the standard deviations of fused ring bond angles (0.3°) versus end phenyl bond angles (0.5°). Standard deviations for bond angles involving hydrogen atoms average 1.5°.

A more detailed discussion of bond lengths and angles for each component of the molecule is presented in a later section.

2. LEAST SQUARES PLANES

Table 9 presents the least squares planes calculated for the individual ring components of the molecule: the central benzene ring, the two imidazole rings, and the two phenyl substituents. In addition, the plane of the entire benzodiimidazole moiety (Plane 1) has been calculated and has revealed an essentially planar fused ring system. The standard deviation of this plane is 0.0048Å. Atomic displacements range from -.008Å to .008Å, while displacement of hydrogen atoms bonded to atoms in the central ring system range from -0.05Å to 0.06Å.

The atoms in the substituent phenyl rings show greater deviation from the plane, with atomic displacements ranging from -0.008 to 0.008Å for plane 3; and from -0.015 to 0.013Å for the plane 2. Hydrogen atom displacements range from -0.11Å to 0.24Å. The standard deviation for the C19-C24 plane is 0.007; for the C13-C18 plane, 0.010.

The acute dihedral angles between the plane of the central benzene ring and those of the fused imidazole are 0.10 and 0.4°, respectively.

The phenyl ring planes are twisted in the same direction from coplanarity with the central benzodiimidazole moiety by 6.0 and 7.9°, respectively. The slight torsion angles are probably attributable to crystal packing forces rather than steric hindrance, as the intramolecular contacts between the nitrogen atoms and adjacent ortho hydrogen atoms average 2.62Å, which is close to the normal van der Waals separation of 2.7Å.

TABLE 7

BOND DISTANCES (Å) AND STANDARD DEVIATIONS
IN BENZODIIMIDAZOLE MODEL COMPOUND

N_1-C_2	1.356(4)	C_{19}-C_{20}	1.386(5)
C_2-N_3	1.333(5)	C_{20}-C_{21}	1.382(4)
N_3-C_{10}	1.399(3)	C_{21}-C_{22}	1.375(6)
C_4-C_{10}	1.383(5)	C_{22}-C_{23}	1.379(6)
C_4-C_{11}	1.369(4)	C_{23}-C_{24}	1.390(4)
C_{11}-C_{12}	1.428(5)	C_{19}-C_{24}	1.385(5)
N_5-C_{11}	1.401(4)	N_1-H_1	0.89(3)
N_5-C_6	1.333(4)	C_4-H_4	0.94(3)
C_6-N_7	1.359(5)	N_7-H_7	0.87(3)
N_7-C_{12}	1.381(3)	C_8-H_8	0.95(3)
C_8-C_{12}	1.374(4)	C_{14}-H_{14}	0.92(3)
C_8-C_9	1.376(4)	C_{15}-H_{15}	1.00(3)
C_9-C_{10}	1.425(5)	C_{16}-H_{16}	0.98(2)
N_1-C_9	1.379(3)	C_{17}-H_{17}	0.96(3)
C_2-C_{13}	1.468(4)	C_{18}-H_{18}	0.93(3)
C_{13}-C_{14}	1.387(6)	C_{20}-H_{20}	0.87(3)
C_{14}-C_{15}	1.376(4)	C_{21}-H_{21}	0.96(3)
C_{15}-C_{16}	1.374(6)	C_{22}-H_{22}	1.09(2)
C_{16}-C_{17}	1.375(7)	C_{23}-H_{23}	0.97(3)
C_{17}-C_{18}	1.387(5)	C_{24}-H_{24}	0.99(3)
C_{13}-C_{18}	1.378(6)		

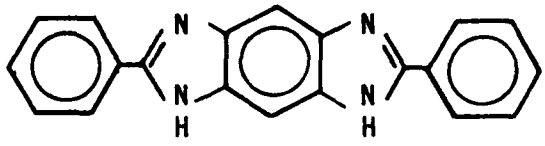
TABLE 8

BOND ANGLES (°) IN BENZODIIMIDAZOLE MODEL COMPOUND

C_2-N_1-C_9	109.1(3)	C_{19}-C_{24}-C_{23}	120.3(4)
N_1-C_2-N_3	111.6(2)	H_1-N_1-C_2	131(1)
C_2-N_3-C_{10}	105.9(3)	H_1-N_1-C_9	120(1)
C_4-C_{10}-N_3	130.3(3)	H_4-C_4-C_{10}	121(1)
C_4-C_{10}-C_9	120.7(3)	H_4-C_4-C_{11}	122(1)
N_3-C_{10}-C_9	109.0(3)	H_7-N_7-C_6	125(2)
C_{10}-C_4-C_{11}	117.0(4)	H_7-N_7-C_{12}	126(2)
C_4-C_{11}-N_5	130.5(3)	H_8-C_8-C_9	127(1)
N_5-C_{11}-C_{12}	108.6(2)	H_8-C_8-C_{12}	119(1)
C_4-C_{11}-C_{12}	120.9(3)	H_{14}-C_{14}-C_{13}	119(2)
C_6-N_5-C_{11}	106.0(3)	H_{14}-C_{14}-C_{15}	119(2)
N_5-C_6-N_7	111.9(2)	H_{15}-C_{15}-C_{14}	120(1)
C_6-N_7-C_{12}	108.6(3)	H_{15}-C_{15}-C_{16}	121(1)
N_7-C_{12}-C_8	131.7(3)	H_{16}-C_{16}-C_{15}	121(2)
N_7-C_{12}-C_{11}	104.9(3)	H_{16}-C_{16}-C_{17}	118(2)
C_8-C_{12}-C_{11}	123.5(3)	H_{17}-C_{17}-C_{16}	121(2)
C_9-C_8-C_{12}	114.5(3)	H_{17}-C_{17}-C_{18}	119(2)
N_1-C_9-C_8	132.1(3)	H_{18}-C_{18}-C_{13}	118(1)
C_8-C_9-C_{10}	123.4(3)	H_{18}-C_{18}-C_{17}	121(1)
N_1-C_9-C_{10}	104.5(2)	C_{19}-C_{20}-H_{20}	120(2)
N_1-C_2-C_{13}	123.0(3)	H_{20}-C_{20}-C_{21}	119(2)
N_3-C_2-C_{13}	125.4(3)	C_{20}-C_{21}-H_{21}	117(1)
C_2-C_{13}-C_{14}	121.1(3)	H_{21}-C_{21}-C_{22}	123(1)
C_2-C_{13}-C_{18}	120.3(3)	C_{21}-C_{22}-H_{22}	123(2)
C_{13}-C_{14}-C_{15}	121.0(4)	H_{22}-C_{22}-C_{23}	117(2)
C_{14}-C_{15}-C_{16}	119.7(4)	C_{22}-C_{23}-H_{23}	121(1)
C_{15}-C_{16}-C_{17}	120.2(3)	H_{23}-C_{23}-C_{24}	118(2)
C_{16}-C_{17}-C_{18}	119.8(4)	C_{23}-C_{24}-H_{24}	124(1)
C_{13}-C_{18}-C_{17}	120.6(4)	H_{24}-C_{24}-C_{19}	115(1)
C_{14}-C_{13}-C_{18}	118.6(3)		
N_5-C_6-C_{19}	125.4(3)		
N_7-C_6-C_{19}	122.7(3)		
C_6-C_{19}-C_{20}	120.8(3)		
C_6-C_{19}-C_{24}	121.0(3)		
C_{19}-C_{20}-C_{21}	121.2(4)		
C_{20}-C_{21}-C_{22}	120.5(4)		
C_{21}-C_{22}-C_{23}	118.8(3)		
C_{22}-C_{23}-C_{24}	121.0(4)		
C_{20}-C_{19}-C_{24}	118.2(3)		

TABLE 9

LEAST SQUARES PLANES AND TWIST ANGLES



Plane 3 Plane 1 Plane 2

Equation of the Plane*	
Plane 1	-3.5572x + 16.6240y - 3.4823z = 3.0684
Plane 2	-4.3989x + 15.7519y - 2.7658z = 3.1459
Plane 3	-4.4395x + 17.0610y - 2.1935z = 4.3429

Plane 1:	Deviations x 10^{+3} σ = 0.0048		
N1	-4.1	N7	-5.3
C2	-0.2	C8	7.7
N3	-5.1	C9	1.7
C4	0.8	C10	1.6
N5	5.7	C11	2.6
C6	-8.5	C12	3.1

Plane 2:	Deviations x 10^{+3} σ = 0.0103
C13	1.7
C14	-4.0
C15	-3.5
C16	13.3
C17	-15.6
C18	8.1

Plane 3:	Deviations x 10^{+3} σ = 0.0067
C19	8.4
C20	-8.6
C21	5.8
C22	-2.7
C23	2.7
C24	-5.6

Twist Angles
Plane 1 - Plane 2: 6.0°
Plane 1 - Plane 3: 7.9°

*x, y and z are fractional coordinates in direct space. The deviations and coefficients of each coordinate are in Angstroms.

3. THE MOLECULE

A mean carbon-carbon bond distance of 1.395Å, with a root mean square deviation of 0.002Å is found in the central benzene ring whereas the corresponding value for the end phenyl groups is 1.381Å, with an rms deviation of 0.006Å.

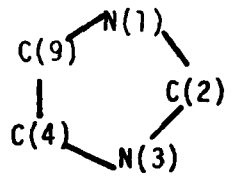
Table 10 lists ring dimensions for several imidazoles taken from the literature. Comparison of the four carbon-nitrogen lengths in this investigation with values in Table 10 shows that all bonds are within the expected range for a delocalized imidazole system.

The imidazole moieties in the model compound, however, can be seen to be slightly asymmetrical about a line passing through the apical carbon, C2 or C6, and bisecting the opposite bond. The difference between the N1-C2 and N3-C2 bond is 0.023Å (roughly four times the estimated standard deviation); between the N5-C6 and N7-C6 bonds, 0.026Å. There is also an associated difference of 3.2° between the C2-N3-C10 and C2-N1-C9 bond angles, and of 2.6° between the C6-N5-C11 and C6-N7-C12 bond angles. Though moderate, these differences point to a semi-localization of the carbon-nitrogen double bond on the pair with the shorter bond distance, which is consistent with the observation that hydrogens H1 and H7 are bonded to N1 and N7, respectively.

Semi-localization of the carbon-nitrogen double bond is characteristic of some benzimidazoles. Selected bond lengths and angles for these benzimidazoles are compared in Table 11. Table 11 also lists benzimidazoles in which π electron density is delocalized over the imidazole ring, as is apparently the case with 2-mercaptobenzimidazole. The compound exists as one of two tautomers, a thiol (I) or a thione (II). The resonance structures are drawn for each tautomer, excluding resonance structures contributed from the benzene ring. The negative charge on nitrogen in resonance structure (b) makes it an unlikely contributor to resonance stabilization of structure I. The number of favorable resonance contributors to structure II, however, predicts this structure to be thermodynamically favored over structure I.

TABLE 10

SELECTED IMIDAZOLE RING DIMENSIONS (Å)



	N(1)-C(2)	C(2)-N(3)	N(3)-C(4)	C(4)-C(9)	C(9)-N(1)	Reference
Imidazole at -150°C	1·326	1·349	1·369	1·358	1·378	(23)
Imidazole at 24°C	1·311	1·337	1·372	1·311	1·381	(24)
6-mercaptopurine monohydrate	1·352	1·333	1·368	1·394	1·373	(25)
Hypoxanthine hydrochloride	1·333	1·318	1·376	1·368	1·375	(26)
1,3-dimethyl-2(3H)-imidazolethione	1·35	1·35	1·41	1·31	1·41	(27)
2-mercaptobenzimidazole	1·362	1·362	1·383	1·400	1·383	(28)
2,6-diphenyl(1,2-d; 5,4-d')benzodiimidazole	1·356	1·333	1·399[a]	1·425[a]	1·379	(this work)

[a]These distances refer to the N(3)-C(10) and C(9)-C(10) bonds in the model compound.

TABLE 11

COMPARISON OF SELECTED BOND LENGTHS AND ANGLES OF SEVERAL BENZIMIDAZOLES

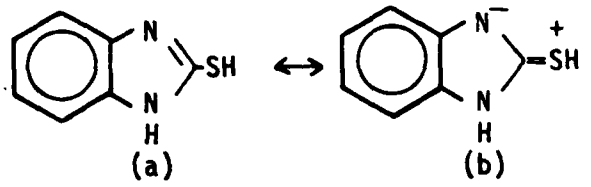
Compound	(Ref)	Bond Length (Å)		Bond Angle (°)	
		N_1-C_2	N_3-C_2	C-N_1-C	C-N_3-C
2-mercaptobenzimidazole (I, II)*	(28)	1.362(6)	1.362(6)	110.4(4)	110.4(4)
2-thio-1-(β-D-ribofuranosyl)-3-H-benzimidazole (III)**	(29)	1.344(5)	1.377(5)	110.9(3)	109.4(3)
2-chloro-1-(β-D-ribofuranosyl)-benzimidazole (IV)***	(30)	1.293(7)	1.367(8)	104.4(4)	104.1(4)
Benzimidazole-benzimidazolium fluoroborate salt (protonated) (V)	(32)	1.320(3)	1.338(4)	109.1(2)	109.8(2)
Benzimidazole-benzimidazolium fluoroborate salt (non-protonated)	(32)	1.306(3)	1.364(3)	105.5(2)	106.9(2)
Benzimidazole	(31)	1.311(4)	1.346(5)	106.6(3)	104.2(2)
Imidazole 5,5-diethyl barbituric acid complex	(33)	1.300(3)	1.324(4)	105.2(2)	107.0(2)
2,6-diphenyl (1,2-d; 5,4-d')benzodiimidazole	(this work)	1.356(5)	1.333(5)	109.2(3)	106.0(3)

*C=S bond length, 1.671(8)Å

**C=S bond length, 1.693(4)Å

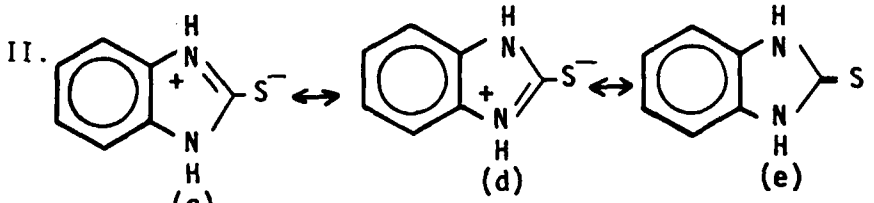
***C=S bond length, 1.768(8)Å

I.



(a) (b)

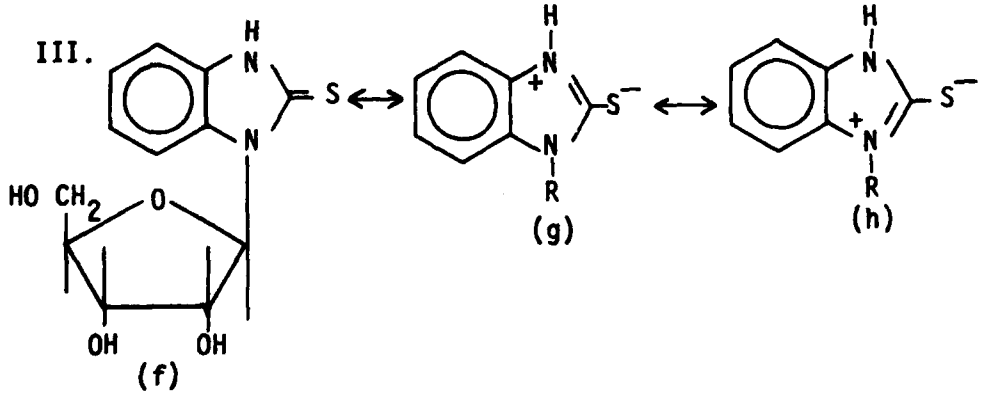
II.



(c) (d) (e)

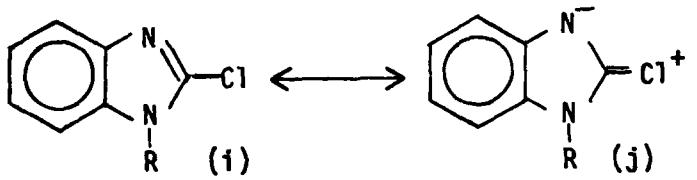
The crystal structure determination of 2-mercaptobenzimidazole (Reference 28) shows hydrogen atoms covalently bonded to both nitrogen atoms, equivalent C-N and C-N bond lengths intermediate between single and double bonds, and a carbon-sulfur double bond, which confirms structure II as the preferred tautomer. 2-thio-1-(β-D-ribofuranosyl) 3-H-benzimidazole (III) is similar to mercaptobenzimidazole in that the apical carbon is double bonded to sulfur (Reference 29). The presence of an electron donating group, ribofuranosyl, increases the thermodynamic favorability of (g) and makes it a stronger contributor to resonance. Hence, though the imidazole ring is still delocalized, one C-N bond will be slightly shorter than the other. There is an 0.033Å difference between the C2-N1 and C2-N3 bond lengths.

III.



(f) (g) (h)

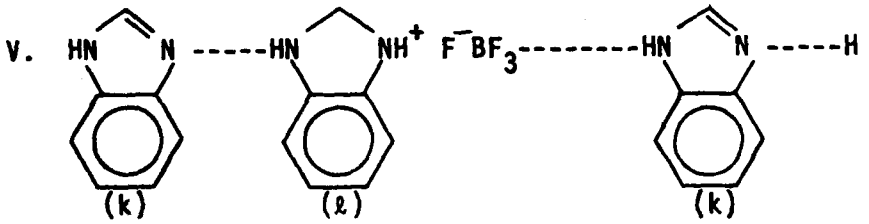
In contrast, the chloro analog of 2-thio-1-(β-D-ribofuranosyl) benzimidazole (IV) shows semi-localization of the carbon-nitrogen double bond, with a 0.074Å difference between the C2-N1 and C2-N3 bond lengths (Reference 30).

IV. 

The positive charge on chlorine in resonance structure (j) makes it a very weak contributor to resonance stabilization.

Benzimidazole has a tendency to form intermolecular hydrogen bonds. The involvement of the electron lone pair on nitrogen in hydrogen bonding lessens its contribution to the π system in the ring. This would explain in part the apparent semi-localization of electron density on the C2-N1 bond in benzimidazole (Reference 31). The difference in C-N bond lengths is 0.035Å.

An interesting example of the effect of environment on the delocalization of the imidazole ring is the benzimidazole-benzimidazolium fluoroborate salt (Reference 32), in which the fluoroborate anion forms a salt with one benzimidazole cation.

V. 

Thus (k) is in an environment similar to intermolecular hydrogen bonded benzimidazoles, with a marked difference in C-N bond lengths (0.058Å). The protonated form (ℓ), on the other hand, has hydrogen atoms covalently bonded to each nitrogen, delocalizing the ring and minimizing differences in bond lengths (0.018Å).

The extent of semi-localization in the diimidazole model compound may now be qualitatively evaluated in terms of the correlation between the extent of semi-localization and the difference in C-N bond lengths. Compared to other benzimidazoles cited, one concludes that the imidazole ring in the model compound exhibits only a slight degree of semi-localization of the C-N double bond, due to extensive hydrogen bonding of all four nitrogen atoms with solvent water molecules. This is similar to that observed for 5,5-diethylbarbituric acid - imidazole complex, which experiences hydrogen bonding between NH---N on the imidazole (Reference 33). The bond length difference between C2-N1 and C2-N3 is slight at 0.024Å.

It would be shortsighted to use bond length differences alone to determine whether a system is semi-localized or not. Such factors as the contributions to resonance, environment of the molecule, and opportunity for hydrogen bonding must be taken into account.

The quantitative determination of delocalization in a system depends on calculation of bond orders. In an analysis of imidazo-[1,2-b]-as-triazine (Reference 34), simple LCAO calculations were used to correlate bond orders with bond lengths to evaluate the extent of semi-localization in a system where comparison of bond lengths was not a sufficient determinant. Least squares fit of the reported bond lengths vs bond orders in Figure 2 of Reference 34 produces a linear function with the equation $y = -4.57x + 6.808$, where y is the bond order and x is the bond length, with a standard deviation 0.168 and a correlation coefficient -.517. A comparison of the results of the imidazo-[1,2-b]-as-triazine study with carbon-nitrogen bonds reported in this investigation calculates a bond order of 0.718 for the N3-C2 bond and of 0.613 for the N1-C2 bond, on a scale where .500 is the bond order of a single bond, 1.000 is the bond order of a double bond. The calculated bond orders indicate that both carbon-nitrogen bonds are higher than single bond order, with the N3-C2 bond possessing more double bond character than the N1-C2 bond.

The difference in the C9-N1-C2 and C10-N3-C2 bond angles is reflected in larger N3-C10-C9 and N5-C11-C12 bond angles (109.0°, 108.6°, respectively) and smaller N1-C9-C10 and N7-C12-C11 angles (104.5° and

104.9° respectively). The other C-N bonds, N1-C9, N3-C10, N5-C11 and N7-C12, appear roughly equivalent at about 1.379Å to 1.401Å.

Another significant feature of the diimidazole structure is the cis orientation of the lone pair nitrogen atoms. The nonstereo-specific synthesis should result in a crystalline product that contains both isomers. A mixture of isomers most probably would lead to disorder in the structure; fortunately, disorder was not a serious problem in this investigation. An explanation for the preferential isolation and crystallization of one isomer over another is discussed in the next section.

4. WATER STRUCTURE

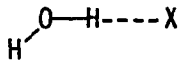
An early indication of the presence of solvent in the crystal was the difference between the calculated and measured densities (1.07 g/cc and 1.31 g/cc respectively). Both the ethanol-grown and sublimed crystals appeared to contain solvent since their measured densities were comparable to each other. Difficulties experienced by synthetic polymer chemists in drying polybenzimidazoles (Reference 13) suggested that these compounds strongly attract water. The strength of this attraction was demonstrated by the fact that in the crystallization of the model compound water was carried over with the material in the sublimation process. Thermogravimetric/Mass Spectrometric (TGA) analysis showed a substantial weight loss (≃ 30%) at 375° attributed mainly to water. The stability of the crystals in air at room temperature and normal humidity indicated that the water present was incorporated into the crystal lattice rather than merely absorbed through the surface.

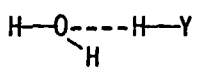
Refinement of the structure confirmed the presence of 16 water molecules per unit cell. Elucidation of the water network gave a possible explanation for the preferential crystallization of the cis isomer over the trans isomer. Perhaps the hydrogen bonded network of the cis isomer provides a crystalline structure that is more efficiently packed and hence favored over a possible structure involving the trans isomer. Additionally, the preference of water for the cis isomer could affect the solubility of both isomers, leading to an unexpected separation of the two isomers during purification and recrystallization of the crude product.

It is probable that the sublimed crystal also involves the cis isomer exclusively. Density measurements indicate that the sublimed crystals are also hydrated. It is possible that any water present in the crude material was carried over in the sublimation process to form the hydrate of the cis isomer, while the starting material left in the bottom of the sublimation apparatus may have been a mixture of the trans isomer and impurities.

Survey Weissenberg and precession photographs show that the sublimed crystal belongs to the same space group ($P2_1/c$) as the ethanol grown crystal. A cursory comparison of a limited diffractometer data set collected on the sublimed crystal with data collected on the ethanol-grown crystal shows little difference in the relative magnitude of intensities for selected reflections. This indicates that the cis isomer and accompanying water structure persist in crystals grown by sublimation, although a more detailed comparison of the two structures would require a full, three-dimensional structure determination of the sublimed material.

Solvent water molecules in the ethanol grown crystal form hydrogen bonds bridging molecules related by an inversion center. Surprisingly, hydrogen bonding between molecules related by a glide plane is not observed. The network makes maximal use of the four coordination sites on each water molecule. At least three sites are engaged on each water molecule; in the case of O1 and O3, all four coordination sites are occupied. Each water acts as both a hydrogen bond donor (illustrated in (a)) and a hydrogen bond acceptor (illustrated in (b)).

(a) 

(b) 

Donor-acceptor relationships for each water are detailed in Table 12.

Four water molecules in the asymmetric unit link N3 and N5 to form a large ring (Figure 4). The ring bends over the molecule, with the best plane containing atoms N3-O4-O1-N5 inclined 37° to the benzodiimidazole plane. The best plane through O4-O2-O3-O1 makes roughly a 53° angle with

TABLE 12

DONOR-ACCEPTOR RELATIONSHIPS AND CONTACT DISTANCES (Å) FOR WATER MOLECULES

Atom	Donor	Acceptor	Symmetry Operation	Contact Distance
O_1	O_1	N_5*	2	2.837(4)
	O_3*	O_1	2	2.755(3)
	O_1	N_3*	4	2.808(4)
	O_3*	O_1	6	2.796(3)
O_2	O_2	O_3*	2	2.819(4)
	O_2	O_4*	2	2.734(3)
	N_7*	O_2	5	2.835(5)
O_3	O_3	O_1*	2	2.755(3)
	O_3	O_1*	6	2.796(3)
	N_1*	O_3	1	2.881(4)
	O_2*	O_3	2	2.819(4)
O_4	O_4	N_3*	2	3.081(4)
	O_4	N_5*	4	3.084(5)
	O_2*	O_4	2	2.743(3)

Symmetry Operations: If the atom has fractional coordinates of x, y, z, then atom is located at the coordinates indicated by each symmetry operation:

Sym Op	Fract Coord	Sym Op	Fract Coord
1	x y 1+z	5	-x 1-y 2-z
2	x y z	6	-x 1-y 1-z
4	1-x 1-y 2-z		

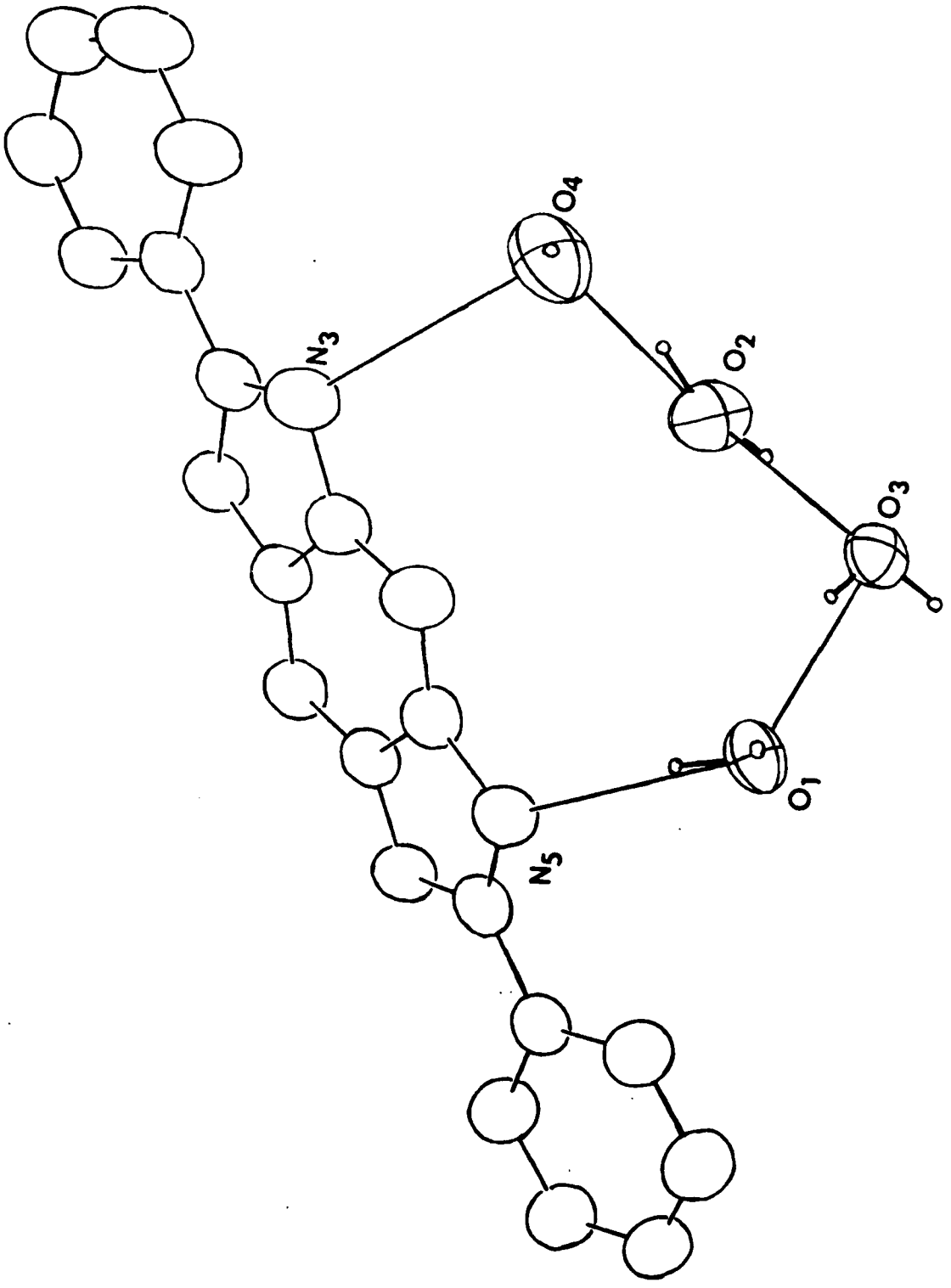


Figure 4. The Four Hydrogen Bonded Water Molecules in the Asymmetric Unit Bridging N3 and N5 of the Benzodiimidazole Segment, Viewed Approximately Down c.

the N3-O4-O1-N5 plane. Table 13 lists bond lengths and angles for water molecules. The average O-H bond is 0.83A; the average H-O-H bond angle is 108°. The O3-H06 bond length is especially short at 0.72Å, while the H-O1-H bond angle of 98° is somewhat smaller than the normal value. Contact distances range from 2.734Å to 3.084Å, within the expected range for hydrogen bonds.

TABLE 13

BOND DISTANCES (Å) AND BOND ANGLES (°) AND STANDARD DEVIATIONS IN BRIDGING WATER STRUCTURE

O1-H01	1.01(3)	H01-O1-H02	98(2)
O1-H02	0.81(2)	H03-O2-H04	116(2)
O2-H03	0.82(2)	H05-O3-H06	112(2)
O2-H04	1.22(2)		
O3-H05	1.00(2)		
O3-H06	0.72(2)		
O4-H07	0.86(3)		

When viewed along a, molecules related by a center of symmetry at (½½0) are stacked such that O1 and O4 of one molecule hydrogen bonds with $N3^{\dagger}$ and $N5^{\dagger}$, respectively, of the other molecule. († denotes atoms related by an inversion center to those in the asymmetric unit.) Thus, two four-membered rings are formed whose contact distances are comparable to those in the asymmetric unit. Figures 5 and 6 show the water structure of a pair of molecules related by an inversion center. O1 is a hydrogen bond donor to N5 and $N3^{\dagger}$, and O4 is a hydrogen bond donor to N3 and $N5^{\dagger}$. In addition, hydrogen bonds along a link O2 with $N7^{\dagger}$ of another molecule related by another inversion center at (0½0), with N7 acting as a hydrogen bond donor.

When viewed along c, molecules related by a center of symmetry at (0½½) are bridged by hydrogen bonds between O1 and O3 to $O3^{\dagger}$ and $O1^{\dagger}$, forming still another four-membered ring composed solely of water molecules. Contact distances in the ring are 2.755 and 2.796Å. Absent in Figures 5 and 6 are the additional hydrogen bonds between O3 and $N1^{\dagger}$, and O2 and $N7^{\dagger}$ mentioned above.

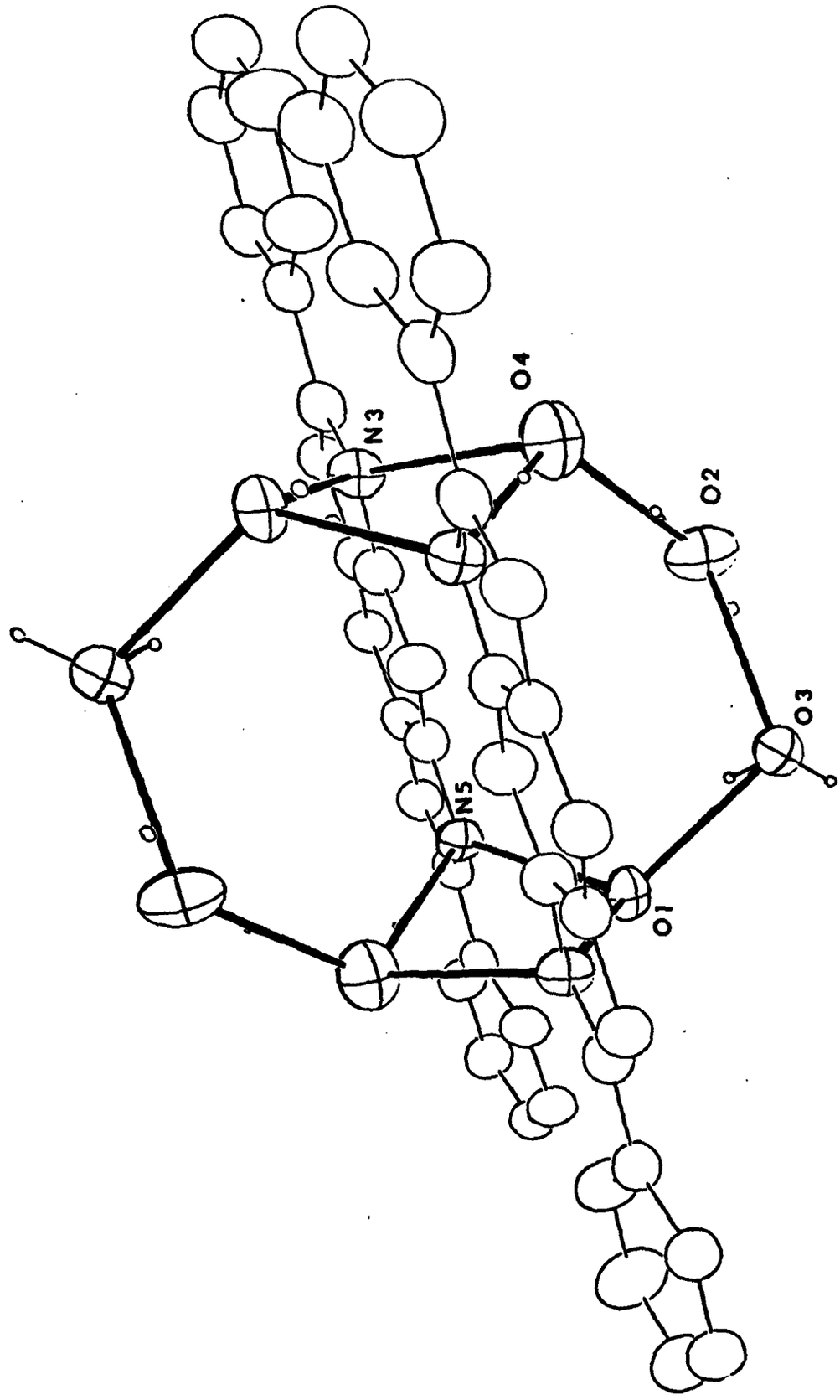


Figure 5. Water Structure of a Pair of Molecules Related by an Inversion Center Viewed Approximately Down a.

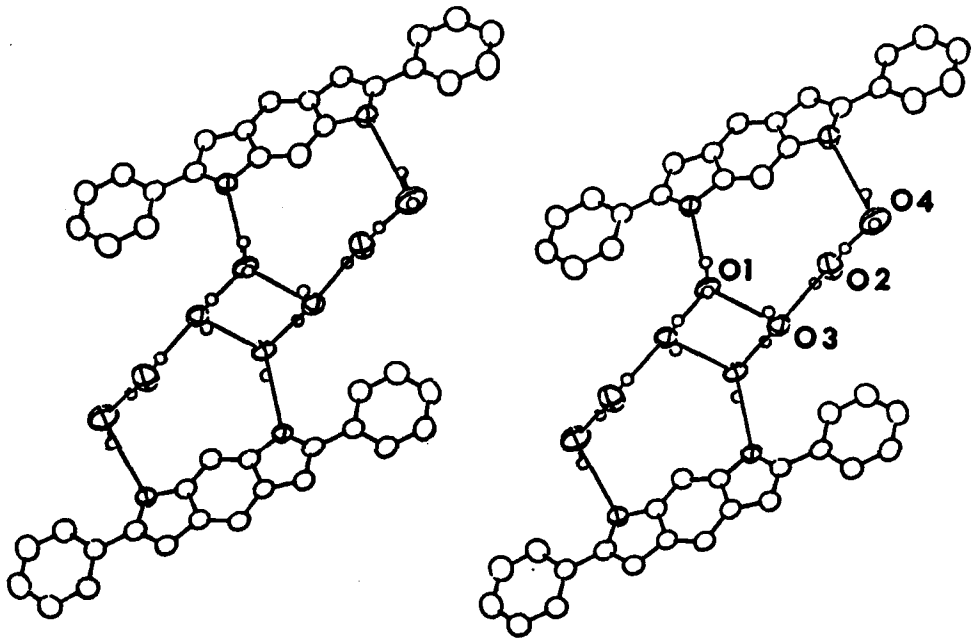


Figure 6. Stereoview of Water Structure of a Pair of Molecules Related by an Inversion Center, Viewed Approximately Down c.

5. PACKING

The c glide plane perpendicular to b generates two vertical columns of molecules of different orientation, characteristic of a herringbone pattern. The molecules are inclined at an angle of 48.2^{o} to the b axis. The perpendicular distance between adjacent molecules in a stack is 3.93Å. A stereoview of one unit cell is shown in Figure 7.

Thus, molecules within a particular stack are intricately connected through hydrogen bonds, while weaker van der Waals interactions relate molecules of adjacent stacks. Since no hydrogen bonding occurs between molecules along b, crystals would be expected to cleave most readily perpendicular to b, or parallel to the ac plane. Experience in cleaving ethanol-grown crystals of the model compound confirms these predictions.

Comparison of Figure 7 with the packing plots of c-bisoxazole (Figure 8) and t-bisthiazole (Figure 9) shows similarities between the three structures. Delocalization of the fused ring system accounts for the high degree of planarity in the c-bisoxazole model compound, but in bisthiazole planarity is precluded by the steric clash between nitrogen and sulfur atoms on the thiazole ring with ortho hydrogen atoms on the phenyl substituents, resulting in a torsion angle of 23.2^{o} between the benzobisthiazole moiety and the phenyl groups.

No hydrogen bonding occurs in c-bisoxazole and t-bisthiazole; packing forces are of the van der Waals type. The low heat of sublimation in c-bisoxazole reflects the absence of significant intermolecular interaction in the crystal.

6. WATER UPTAKE EXPERIMENTS

It has already been noted that the polybenzimidazoles have a high affinity for water. In the case of PDIAB, 379 hours of atmospheric exposure produces an uptake of water of 20.1%, or a pickup of 2.6 moles of water per mole of repeat unit. In a related set of experiments, exposure of a dry sample of PDIAB to a humidity chamber for forty eight hours resulted in a pickup of 30.2%, or 3.9 moles of water per mole of repeat unit. These experiments are in good agreement with the four water molecules per asymmetric unit found in the structure of the diimidazole model compound. Thus, it appears that saturation of available binding sites for water is achieved with four water molecules per polymer repeat unit.

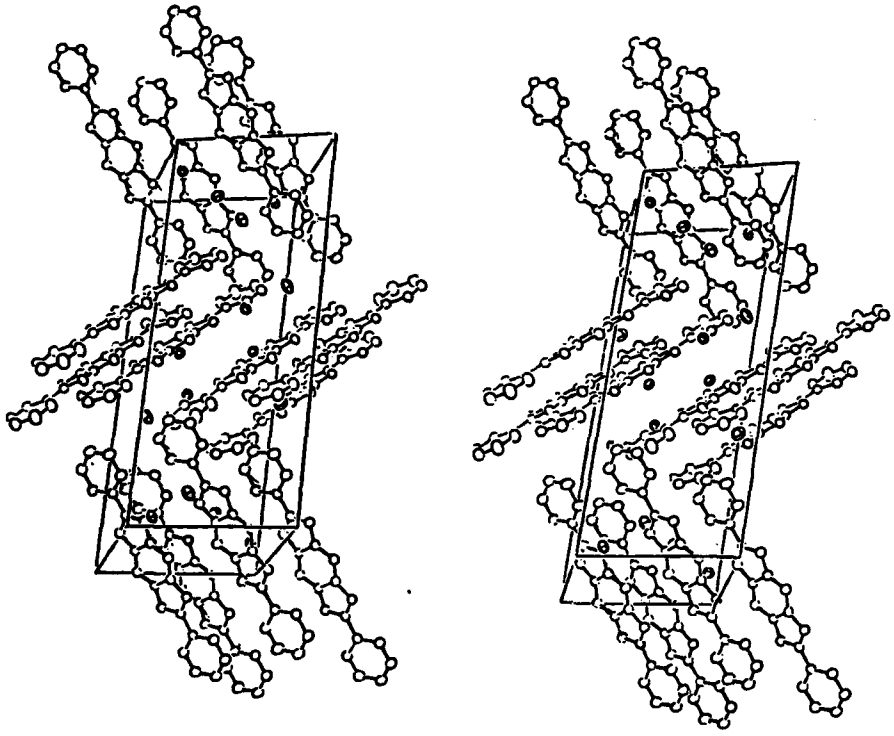


Figure 7. Stereoview Down the Negative a-axis of the Molecular Packing in the Unit Cell. Water molecules are contoured for clarity. The b-axis is vertical.

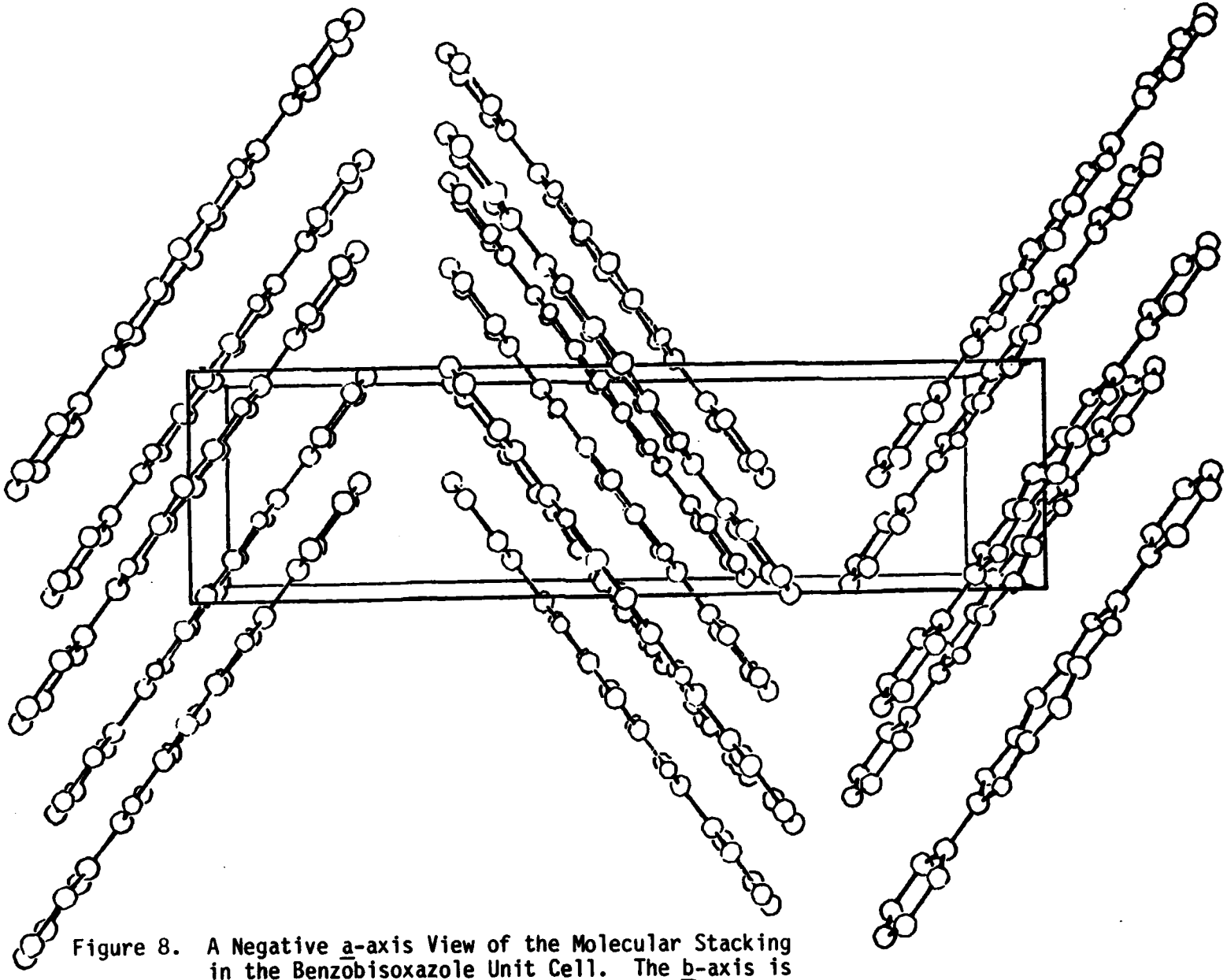


Figure 8. A Negative a-axis View of the Molecular Stacking in the Benzobisoxazole Unit Cell. The b-axis is vertical and the c-axis is horizontal. Taken from Figure 2 of Reference 11.

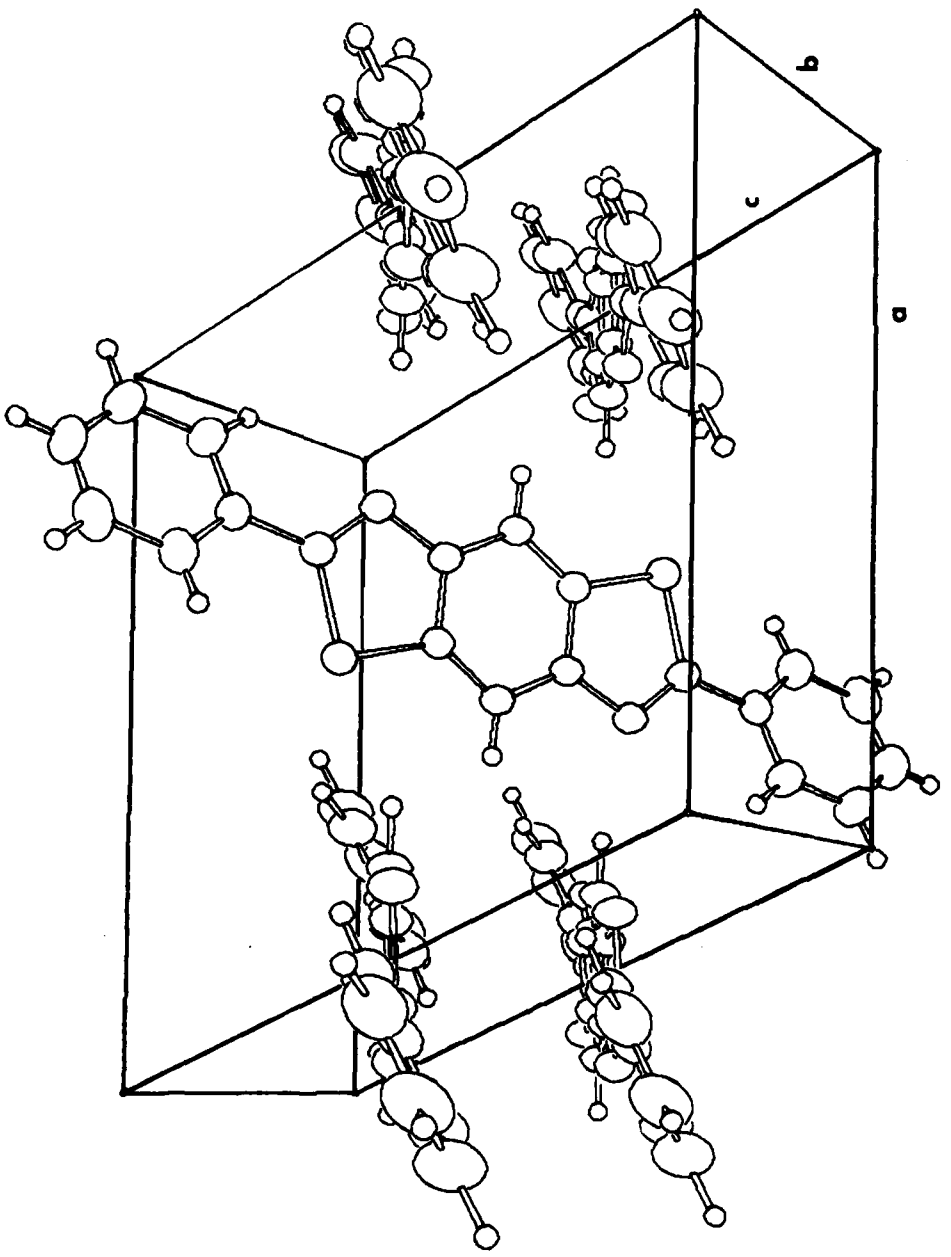


Figure 9. Molecular Stacking in the Benzobisthiazole Unit Cell. The a-axis is horizontal and the c-axis is approximately vertical.

Although repeated heating of PDIAB under vacuum can drive off this water, there is good evidence that much of the chemically bound water remains intact in the solid material.

The retention of water by the diimidazole model compound was examined by thermogravimetric/mass spectral analysis and differential scanning calorimetry. TGA/MS of the impure model compound shows a 30% weight loss at 375°C, 61% at 480°C, and 84% at 915°C. The fairly low ion intensities for this amount of weight loss points to extensive sublimation of the sample. At least three volatile products are detected below 480°C, with water as the principal product.

DSC data indicates higher lattice energies in the diimidazole model compound compared to the PBO and PBT model compounds. Whereas melting endotherms are observed at approximately 300°C for the PBO and PBT model compounds (the T_m of c-bisoxazole is obscured by the onset of sublimation), the diimidazole model compound exhibits two broad endotherms at 300° and 480°C, which are not characteristic of melting transitions but indications of the possible loss of water.

7. RELATIONSHIP TO POLYMER FILM AND FIBER DATA

Figure 10 depicts a wide angle x-ray diffraction photograph of poly(p-phenylenebenzodiimidazole) solution cast film. The pattern is interpreted in terms of a sample consisting of randomly ordered crystallites. A very faint outermost ring (visible on the photographic negative only) corresponds to an interplanar spacing of 2.4Å. The d-spacing of the prominent broad ring measures 3.97Å, which correlates well with the interplanar spacing calculated for the model compound (3.93Å).

A few d-spacings for some of the more intense reflections in the single crystal study may be calculated for a hypothetical polymer powder pattern. The intense 141 and 210 reflections, with calculated d-spacings of 3.77Å and 3.86Å, respectively, correlate with the measured d-spacing in the solution cast film (3.97Å).

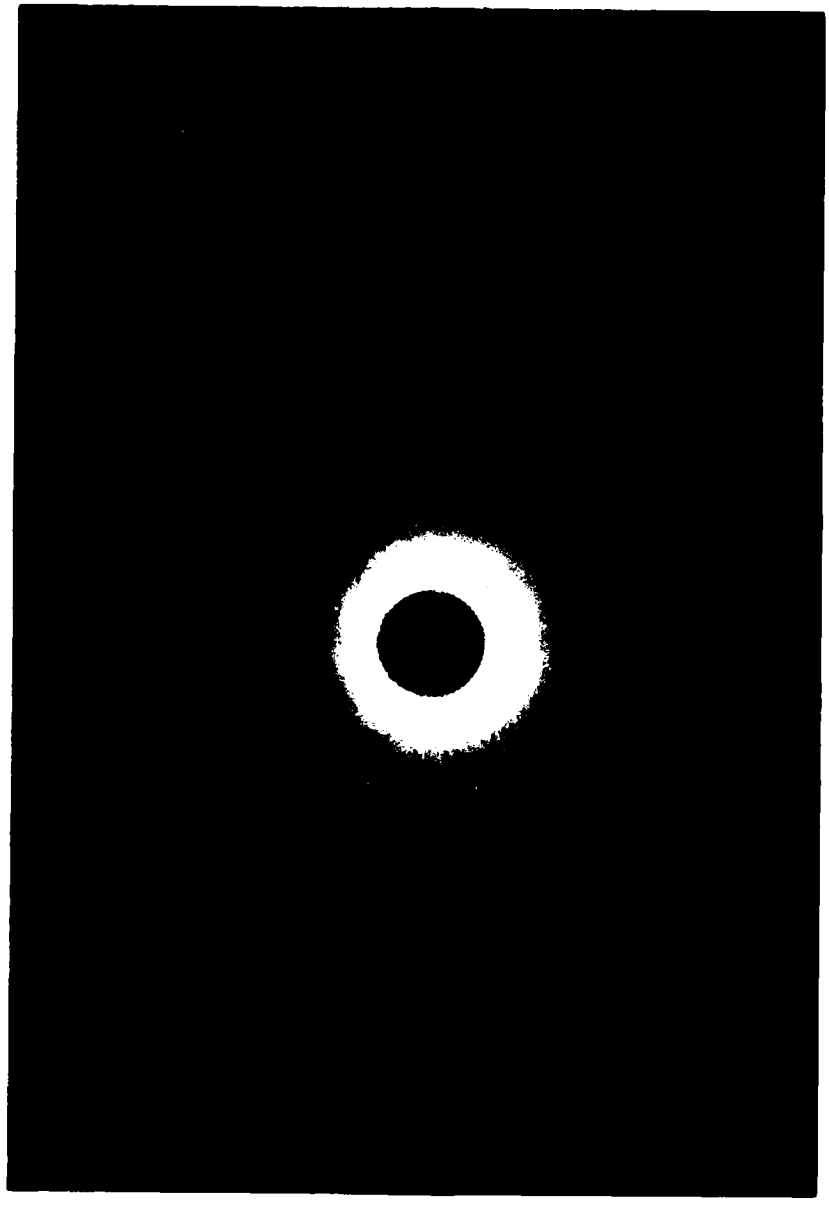


Figure 10. Wide Angle X-Ray Diffraction Pattern of Solution Spun Poly (p-phenylenebenzodiimidazole) Film.

In the absence of any fiber diffraction data for PDIAB, a plausible model for the packing in oriented fibers would involve chains of polymer extending in the direction of elongation, in the manner found for PBT (References 8 and 9). It now seems likely that a hydrogen bonded water structure, which plays such an important role in the crystal packing of the model compound, might serve as lateral connections between polymer chains. Given the increased lattice strength due to these intermolecular forces, it is expected that PDIAB would have a higher T_m than either PBO or PBT, as these polymers would be held in a crystalline lattice solely by van der Waals forces.

8. X-RAY POWDER DIFFRACTION PATTERNS

It was mentioned previously that crystals grown from ethanol and sublimation had similar structures. This conclusion was based on a comparison of unit cell dimensions and uncorrected intensities of a few reflections (Table 1). As a result, powder patterns of both materials should exhibit obvious similarities. It was decided at this point to record Debye-Scherrer photographs of the two materials in order to check for polymorphism. Specimens of both crystals were prepared by grinding prior to being loaded into 0.5 mm glass capillary tubes. The tubes were mounted in a 57.3 mm radius powder camera and irradiated with filtered CuK_α radiation for 48 hours. The crystals grown from ethanol produced a much richer pattern of lines visible out to $2\theta=53^o$. The sublimed sample, on the other hand, did not diffract beyond about $2\theta=38^o$, and lines observed below this angle were sparse and fairly diffuse. The experimental powder patterns are presented in Table 14 and Figure 11. Taking into account the low resolution and overall poor quality of the sublimed pattern compared to the ethanol-grown one, a line-for-line comparison of the two patterns shows them to be in only fair agreement. Unexplained is the discrepancy in the location and intensity of the 7.8Å line (7.38Å in the sublimed pattern), as well as the apparent mismatch in the d-spacing of the 3.76Å line (4.04Å in the pattern of sublimed crystals). In view of the rather convincing evidence presented in Table 1, it would be premature at this point to cite these observed differences in the powder patterns as evidence of polymorphism.

TABLE 14

MEASURED POWDER PATTERNS FOR THE ETHANOL-GROWN AND SUBLIMED SAMPLES

Ethanol-Grown			Sublimed		
2θ(°)	d(meas) (Å)	Intensity[a]	2θ	d(meas)	Intensity[a]
7.8	12.31	43	7.37	12.00	66
11.38	7.78	100	11.99°	7.38	25
12.95	7.84	17	too weak		
14.23	6.72	16	14.74	6.01	22
15.31	5.79	16	too weak		
17.85	4.96	19	18.24	4.86	60
19.26	4.61	22			
21.16	4.19	43	20.99	4.23	48
23.68	3.76	52	21.94	4.04	100
25.08	3.55	31	25.56	3.48	37
26.06	3.42	62			
27.21	3.28	32	27.19	3.28	42
29.03	3.07	23	too weak		
30.10	2.97	12	31.74	2.82	5
33.96	2.64	6			
35.77	2.51	6	36.27	2.48	5
40.88	2.20	6	37.87	2.37	6

[a]Intensities (peak heights) are derived from microdensitometer scans of Debye-Scherrer photographs and are scaled so that the strongest line has an intensity of 100.

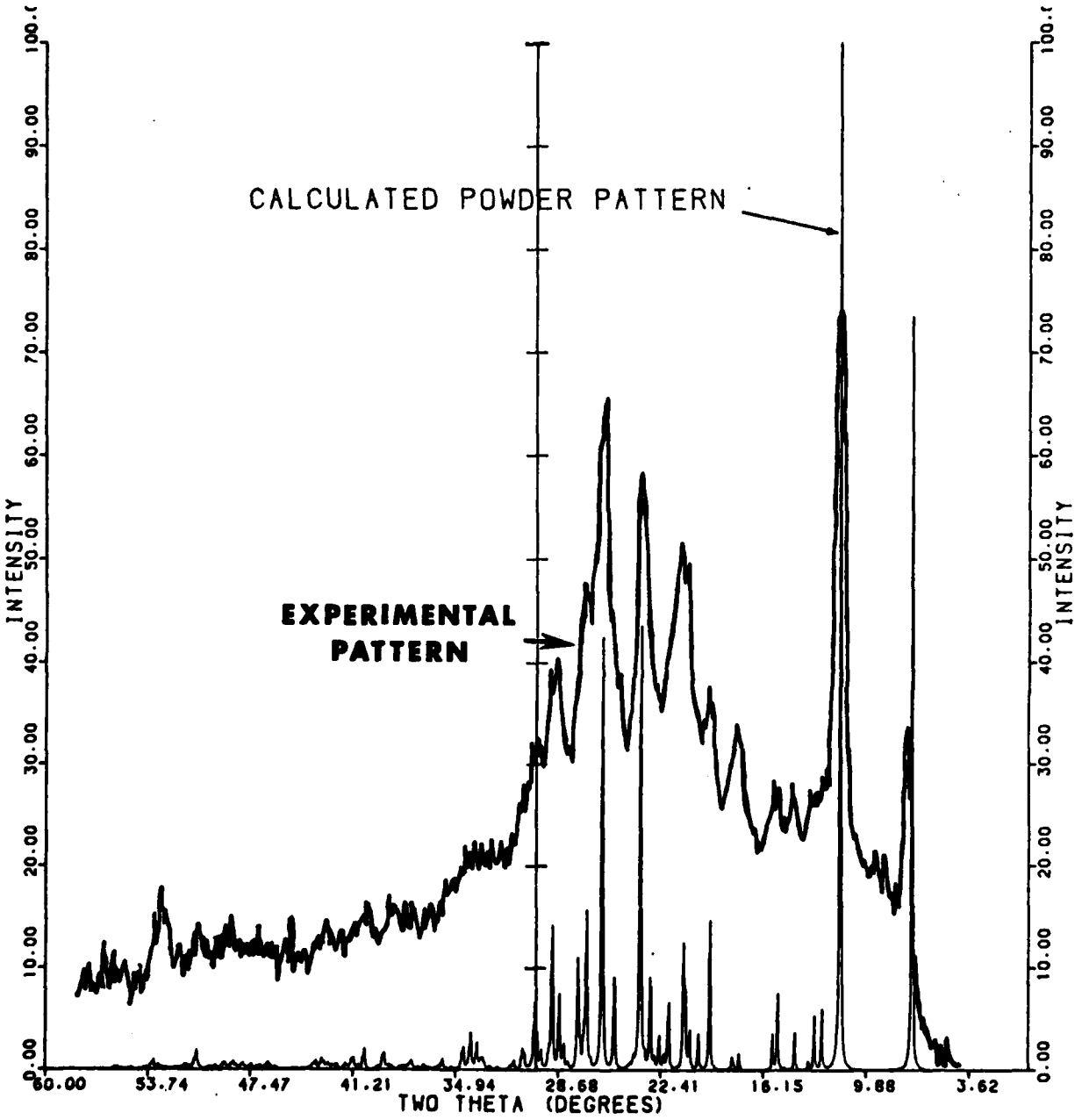


Figure 11. Comparison between the Microdensitometer Scan of a Debye-Scherrer Experimental Powder Pattern for the Ethanol-Grown Crystal and the Computed Powder Pattern using the POWD 7 Program for the Diimidazole Model Compound.

The intense 12.3Å (12.0Å in the sublimed pattern) reflection undoubtedly corresponds to the monomer repeat of 12.197(6)Å in the model compound. The other prominent d-spacings (7.78, 4.86, 4.04, 3.76 and 3.42Å) have interpretations in terms of recurring intramolecular distances and intermolecular chain separations. It should be noted that the broad 4.86, 3.48, and 2.82Å lines in the sublimed pattern appear to be fully resolved in the pattern of the ethanol grown crystals.

9. SIMULATED POWDER PATTERNS COMPUTED WITH POWD 7

The calculation of the simulated Debye-Scherrer pattern for a known crystal structure is possible with Smith and Holomany's POWD 7 Fortran Program. Figure 11 compares the experimental pattern of the diimidazole model compound with the calculated pattern on the basis of the atomic coordinates in Tables 4 and 6 as input parameters. Table 15 lists the d-spacings and intensities as well as to assign hkℓ values to the strongest lines. Excellent agreement is noted not only for the d-spacings, but also for the relative intensities of the lines. In addition, reducing the occupancy of the solvent water molecules from 100 to 50% does not alter significantly the simulated pattern. Thus, it would appear that the integrated intensities of the prominent lines are attributable primarily to the model compound and not to the water structure.

TABLE 15

CORRELATION BETWEEN EXPERIMENTAL AND SIMULATED POWDER PATTERNS AND ASSIGNMENT OF BRAGG hkℓ PLANES FOR STRONGEST LINES

	Experimental Pattern for Ethanol Grown Crystal		Pattern Computed with POWD 7		
hkℓ	d-spacing(Å)	Intensity	d-spacing(Å)	Intensity (100% Occupancy)	Intensity (50% Occupancy)
0 2 0	12.31	43	12.48	63	20
$\bar{1}$ 1 1	7.78	100	7.73	100	100
$\bar{1}$ 4 1	4.96	19	4.95	1	1
$\bar{1}$ 2 2	4.61	22	4.58	16	6
$\bar{2}$ 2 1	4.19	43	4.23	12	5
1 4 1	3.76	52	3.77	53	29
1 5 1	3.42	62	3.43	52	28
2 4 0	3.28	32	3.31	19	10
2 5 0	3.07	23	3.08	16	8

SECTION VI

CONCLUSIONS

1. The crystal structure analysis of the diimidazole model compound has provided molecular structure information applicable to polymeric benzimidazoles in general, and in particular to rod-like benzimidazoles. The structure determination will be useful both for homopolymer structural studies and in the morphology of blends and molecular composites. With renewed interest on the part of the chemical industry aimed at the large scale production of polybenzimidazoles, this work takes on added interest since there is little published data on benzimidazoles and their interaction with water.

2. One can now begin to understand why it has not yet been possible to synthesize high molecular weight, rod-like PBI, specifically PDIAB. At low molecular weight, oligomers crystallize out of polyphosphoric acid (PPA) solution before the condensation polymerization is very far advanced, due to preferential formation of a stable hydrogen-bonded network in the presence of the excess water of condensation. This hydrogen-bonded structure is apparently more energetically favorable than the fully protonated molecular species dissolved in the solvent.

3. PBI's cannot be fully dried under normal drying conditions. Even after days of vacuum oven treatment, 5% or more water is retained in the polymer, as determined by thermogravimetric analysis. Temperatures as high as 350-450^{o}C are required to remove the residual water, at which point the polymer may also begin to degrade. The strong affinity for water is manifested by the ability of PBI's to dry desiccant! Furthermore, the observation that crystals of the model compound grown by sublimation contain the water network is remarkable, implying that water must be carried along with the molecules during the sublimation process. A stoichiometric "limit" of bound water for PDIAB of 30% by weight is the apparent upper limit for water uptake by PBI.

4. It is now more clear why benzoxazoles (PBO) and benzothiazoles (PBT) are not water sensitive. The benzimidazoles have two types of nitrogen atoms, one that is protonated and one that possesses the lone electron

pair. In order to form a stable water network both types are apparently necessary, one functioning as a proton donor and the other as a proton acceptor. PBO's and PBT's have only lone pair electron nitrogen atoms, and in addition, the increased delocalization present in the heterocyclic rings may contribute to the lack of hydrogen bonding to water. The variation in the strength of the hydrogen bonds in PBI's probably results in the reversibility of water uptake, since some of the bonds can be more easily broken than others.

5. This work makes possible certain predictions concerning the structure of PBI polymer:

a) Fibers or films spun from concentrated dopes of high molecular weight PDIAB in PPA would be highly oriented and should exhibit three dimensional crystallinity. They would have similar or somewhat improved modulus compared to PBT, but with higher tensile strength and significantly higher lateral strength and compressive modulus, due to the formation of a hydrogen-bonded water network laterally linking polymer molecules.

b) PDIAB bulk material should have a significant energy absorption mechanism due to the hydrogen-bonded water molecules. For example, an infrared or ultraviolet laser beam would have to deposit much more energy to damage this polymer backbone than for PBT or PBO, since the loss of water would itself dissipate a great deal of absorbed energy. Similarly, PDIAB should also act as a radar absorbing material.

c) The problem of water retention in PBI's would be partially eliminated by the placement of appropriate substituents on the imidazole nitrogen atoms. This would allow PBI to be used as a structural material without the dimensional changes caused by the binding of water.

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APPENDIX - TABLE 3
OBSERVED AND CALCULATED STRUCTURE FACTORS (X10)

-12,0,L

6	66	-52

-12,1,L

6	15	-10
7	0	-11

-12,2,L

6	32	-27
7	16	6

-12,3,L

6	45	-39
7	28	26

-11,0,L

4	27	37
6	43	36
8	0	-7

-11,1,L

2	26	3
3	33	-34
4	12	-12
5	27	13
6	32	-21
7	15	6
8	15	5
9	38	-44
10	5	-24

-11,2,L

2	0	2
3	52	-50
4	11	-24
5	48	-48
6	52	35
7	69	56
8	34	-23
9	26	-19
10	87	88

-11,3,L

2	10	21
3	0	0
4	0	-24
5	42	44
6	28	-8
7	37	-33
8	17	-19
9	36	-26
10	67	53

-11,4,L

2	32	-6
3	59	-60
4	4	-15
5	24	-4
6	35	-20
7	49	-48
8	50	-50
9	0	32
10	65	68

-11,5,L

2	44	34
3	31	23
4	23	-8
5	88	97
6	0	12
7	57	-46
8	23	-6
9	52	-39
10	63	55

-11,6,L

2	35	-42
3	0	-10
4	42	-21
5	9	-4
6	31	-31
7	120	-115
8	40	-29
9	11	-19
10	80	75

-11,7,L

2	51	34
3	24	13
4	0	-10
5	80	81
6	0	-2
7	36	-26
8	16	3
9	34	-29
10	1	-2

-11,8,L

3	30	12
4	20	-16
5	44	-44
6	0	6
7	48	-50
8	8	22
9	21	-22

-11,9,L

3	25	-3
4	21	-14
5	32	44
6	30	-37
7	91	-86
8	0	-1
9	52	42

-11,10,L

3	16	30
4	23	5
5	0	5
6	19	24
7	0	-6
8	46	49
9	19	8

-11,11,L

4	16	5
5	89	-62
6	0	9
7	53	-54
8	20	19

-11,12,L

4	30	-20
5	65	66
6	61	-50
7	21	-22
8	46	43

-11,13,L

5	0	7
6	53	49
7	16	-30

-10,0,L

2	15	-23
4	165	165
6	200	202
8	32	-20
10	50	-59

-10,1,L

1	0	10
2	20	5
3	112	-121
4	47	60
5	13	21
6	0	-5
7	80	-70
8	25	-24
9	31	-19
10	30	10
11	76	69

-10,2,L

1	0	-8
2	40	-32
3	91	84
4	84	89
5	36	-32
6	143	137
7	1	-13
8	20	-22
9	17	24
10	0	0
11	40	-33

-10,3,L

1	2	26
2	0	13
3	40	-32
4	61	60
5	64	50
6	90	-83
7	40	25
8	29	-20
9	50	-47
10	30	25
11	120	131

-10,4,L

1	65	-77
2	50	-53
3	35	16
4	51	-47
5	0	-6
6	90	95
7	44	-44
8	60	-66
9	10	6
10	49	43
11	40	31

-10,5,L

2	46	39
3	35	-43
4	16	19
5	53	53
6	82	-87
7	59	55
8	41	40
9	21	24
10	28	-24
11	3	-4

-10,6,L

1	110	-102
2	27	-16
3	25	17
4	92	-83
5	0	10
6	93	-94
7	0	-19
8	17	5
9	52	40
10	20	-17
11	74	67

-10,7,L

1	55	56
2	32	19
3	54	46
4	45	47
5	104	-113
6	42	43
7	52	-49
8	64	60
9	20	21
10	20	-21
11	25	10

-10,8,L

1	60	-60
2	29	22
3	65	55
4	110	-113
5	17	-29
6	23	-25
7	55	49
8	29	-34
9	0	-9
10	20	-20
11	78	86

-10,9,L

1	41	40
2	30	-13
3	52	32
4	77	76
5	80	-79
6	0	0
7	77	-79
8	29	-22
9	20	-19
10	33	37
11	27	23

-10,10,L

1	27	-19
2	0	9
3	31	10
4	76	-69
5	0	-7
6	100	117
7	43	31
8	53	-47
9	50	-50
10	54	-54

-10,11,L

1	70	61
2	31	-36
3	43	22
4	10	-19
5	65	-64
6	20	-14
7	20	-17
8	71	-64
9	30	24
10	14	-19

-10,12,L

1	0	-20
2	49	38
3	27	-9
4	67	50
5	1	-16
6	30	34
7	43	45
8	41	-34
9	17	-14
10	62	-63

-10,13,L

1	22	-21
2	0	-14
3	47	30
4	40	-43
5	0	0
6	10	3
7	0	-0
8	52	-40
9	35	37
10	20	-3

-10,14,L

2	52	30
3	23	1
4	4	-13
5	37	-43
6	54	51
7	24	20
8	36	-40
9	43	-14

-10,15,L

2	27	-34
3	3	-13
4	39	50
5	31	10
6	30	-20
7	24	29
8	32	-34
9	74	80

-10,16,L

3	5	-16
4	43	-47
5	65	-52
6	34	26
7	21	-4
8	22	-12

-10,17,L

3	41	32
4	49	38
5	26	9
6	43	36
7	13	20
8	37	-40

-10,18,L

4	0	2
5	11	-10
6	44	31
7	40	-30

-9,0,L

2	192	192
4	21	-30
6	32	20
8	137	141
10	96	96
12	50	-59

-9,1,L

1	50	-67
2	62	-53
3	34	-41
4	60	-59
5	60	-69
6	42	35
7	33	30
8	1	11
9	27	-27
10	30	-21
11	7	26
12	76	74

-9,2,L

1	46	-36
2	144	150
3	10	1
4	27	19
5	33	35
6	46	-40
7	283	270
8	39	-36
9	93	87
10	0	-0
11	36	-41
12	26	0

-9,3,L

1	26	-33
2	50	-45
3	15	-24
4	159	-140
5	110	-116
6	35	36
7	11	3
8	93	96
9	0	1
10	37	-30
11	29	-14
12	91	00

-9,4,L

1	21	-21
2	02	99
3	0	-0

-9,4,L

4	56	-68
5	161	154
6	42	-43
7	92	94
8	154	-160
9	58	62
10	21	-4
11	37	-17
12	29	-19

-9,5,L

1	15	-27
2	22	-13
3	16	-1
4	90	-93
5	30	-15
6	33	35
7	217	210
8	132	119
9	22	14
10	33	-34
11	57	-55
12	7	-6

-9,6,L

1	0	-23
2	70	70
3	23	-21
4	27	-21
5	30	39
6	69	-64
7	24	-5
8	92	-82
9	20	-1
10	67	64
11	29	-6
12	29	21

-9,7,L

1	0	34
2	17	-10
3	24	45
4	30	-20
5	229	230
6	35	-29
7	60	64
8	110	97
9	33	-39
10	69	-59
11	10	-23
12	41	34

-9,8,L

1	0	17
2	5	-21
3	41	-39
4	40	-34
5	100	-105
6	52	57
7	15	23
8	0	-12
9	0	-8
10	14	-20
11	3	12
12	60	54

-9,9,L

1	32	31
2	39	34
3	0	0
4	37	-39
5	45	-44
6	50	-53
7	90	35
8	24	23
9	64	-64
10	70	-55
11	0	-19

-9,10,L

1	0	10
2	0	-21
3	22	-5
4	76	-74
5	53	39
6	100	105
7	70	-75
8	0	5
9	30	26
10	44	49
11	23	-2

-9,11,L

1	44	42
2	32	19
3	50	-51
4	50	30
5	103	-170
6	67	-66
7	41	40
8	30	-29
9	37	34
10	53	-40
11	25	-41

-9,12,L

1	42	33
2	44	-31
3	62	52
4	91	77
5	15	27
6	31	9
7	47	-54
8	27	30
9	16	-10
10	31	30
11	10	4

-9,13,L

1	19	-14
2	0	6
3	46	-39
4	60	64
5	55	-44
6	67	-60
7	55	55
8	72	-71
9	26	-39
10	57	-60
11	22	2

-9,14,L

1	23	26
2	27	-12
3	13	-15
4	25	-12
5	0	12
6	11	2
7	40	40
8	41	40
9	101	-95
10	40	-34

-9,15,L

1	2	23
2	29	30
3	14	24
4	46	24
5	31	6
6	30	-17
7	28	25
8	36	-27
9	56	-50
10	39	-28

-9,16,L

1	44	42
2	34	24
3	92	-82
4	0	-14
5	0	22
6	73	-64
7	70	76
8	7	-38
9	66	-64
10	5	7

-9,17,L

1	41	23
2	23	-23
3	56	55
4	49	33
5	27	39
6	69	63
7	24	6
8	0	25
9	45	-41

-9,18,L

1	21	-7
2	46	-36
3	9	-17
4	46	35
5	28	-18
6	72	-76
7	23	27
8	29	-30
9	41	-44

-9,19,L

1	28	-24
2	70	-47
3	0	-1
4	0	-5
5	28	40
6	60	70
7	0	-1
8	14	24

-9,20,L

2	51	-34
3	7	-15
4	32	16
5	43	-44
6	95	-84
7	27	-6
8	0	-0

-9,21,L

4	17	-15
5	82	67
6	33	-22
7	26	-27

-9,22,L

4	57	50
5	16	-26
6	25	-17

-8,0,L

2	105	125
4	103	111
6	411	-408
8	237	245
10	60	-48
12	68	-89

-8,1,L

1	87	-105
2	34	-29
3	216	227
4	52	-51
5	0	-8
6	138	-136
7	126	-127
8	51	-71
9	187	-188
10	53	-60
11	14	26
12	0	9

-8,2,L

1	22	13
2	55	61
3	80	89
4	39	43
5	3	-27
6	29	36
7	52	-47
8	39	-44
9	16	-8
10	51	-55
11	90	-76
12	47	-42

-8,3,L

1	51	-63
2	22	4
3	281	289
4	149	-152
5	69	73
6	190	-196
7	18	7
8	185	-186
9	56	-55
10	60	-68
11	6	-10
12	39	41

-8,4,L

1	19	2
2	37	-46
3	173	181
4	16	-25
5	38	28
6	50	-45
7	15	7
8	61	61
9	46	45
10	28	-29
11	26	-16
12	28	7

-8,5,L

1	130	-131
2	32	-24
3	128	126
4	149	-155
5	122	-113
6	60	59
7	111	113
8	26	6
9	67	69
10	24	-24
11	72	79
12	41	41

-8,6,L

1	31	32
2	38	-48
3	57	60
4	77	-82
5	42	-40
6	205	-212
7	89	85
8	173	177
9	18	1
10	17	4
11	89	-82
12	22	-24

-8,7,L

1	186	-191
2	0	-5
3	112	-101
4	0	8
5	51	-45
6	93	97
7	77	83
8	84	92
9	60	50
10	27	-24
11	51	60
12	29	20

-8,8,L

1	82	81
2	68	-69
3	76	74
4	101	-107
5	103	-100
6	12	19
7	47	-50
8	140	138
9	102	-102
10	0	14
11	81	-83
12	0	-3

-8,9,L

1	0	29
2	28	26
3	44	-33
4	29	-26
5	110	-117
6	137	130
7	50	57
8	142	141
9	0	23
10	35	-36
11	62	53
12	24	-30

-8,10,L

1	0	7
2	103	-106
3	59	66
4	13	7
5	76	-74
6	97	106
7	51	-40
8	45	51
9	54	-54
10	59	60
11	19	2
12	45	32

-8,11,L

1	52	61
2	38	21
3	16	11
4	122	-110
5	15	11
6	97	100
7	66	-72
8	82	83
9	90	-92
10	0	-15
11	0	14
12	21	10

-8,12,L

1	0	-2
2	62	-52
3	29	-16
4	57	66
5	12	38
6	154	158
7	78	81
8	61	-57
9	60	68
10	0	-9
11	13	-12

-8,13,L

1	55	55
2	0	16
3	53	-57
4	28	-26
5	12	4
6	103	-101
7	101	-102
8	3	-1
9	33	-48
10	19	-21
11	31	-11

-8,14,L

1	43	-34
2	28	17
3	15	20
4	32	17
5	40	-51
6	52	48
7	127	130
8	0	-7
9	39	34
10	40	-31

-8,14,L

11	0	-16

-8,15,L

1	61	57
2	28	36
3	40	-19
4	61	62
5	21	27
6	148	-147
7	79	-73
8	0	-26
9	38	-47
10	25	25
11	62	62

-8,16,L

1	58	-54
2	29	23
3	26	14
4	35	-47
5	26	21
6	65	55
7	53	-48
8	52	-57
9	62	61
10	35	38
11	32	-2

-8,17,L

1	41	40
2	21	13
3	0	10
4	88	92
5	122	121
6	101	-94
7	35	-38
8	36	22
9	82	-85
10	28	-1

-8,18,L

1	56	-45
2	6	-30
3	37	-32
4	55	-53
5	0	30
6	5	14
7	69	-67
8	0	7
9	43	47
10	39	-6

-8,19,L

1	35	32
2	16	-13
3	64	60
4	62	55
5	51	45
6	37	-35
7	51	-44
8	29	37
9	24	-4
10	55	-54

-8,20,L

1	30	-31
2	84	83
3	48	42
4	70	-71
5	11	-17
6	9	7
7	21	-7
8	28	35
9	0	-1

-8,21,L

1	0	20
2	0	-6
3	15	10
4	76	74
5	10	16
6	17	-9
7	32	-19
8	42	30
9	27	15

-8,22,L

1	0	13
2	81	74
3	0	-19
4	50	-54
5	0	16
6	16	9
7	0	-8
8	63	45

-8,23,L

1	37	-30
2	32	-35
3	46	-43
4	52	56
5	32	0
6	15	-19
7	31	25

-8,24,L

2	15	-4
3	33	-34
4	50	-47
5	0	-29
6	0	9

-8,25,L

4	27	-24
5	23	15

-7,0,L

2	87	-82
4	87	-89
6	244	-237
8	168	176
10	0	-5
12	91	83

-7,1,L

1	156	161
2	156	150
3	54	49
4	14	20
5	45	38
6	0	-1
7	74	-79
8	0	14
9	67	72
10	28	-37
11	45	-45
12	0	-17
13	0	-13

-7,2,L

1	29	20
2	155	-155
3	2	-25
4	116	-111
5	338	336
6	83	87
7	425	434
8	117	120
9	30	-41
10	59	-61
11	5	-6
12	85	85
13	0	-1

-7,3,L

1	11	26
2	74	77
3	35	-31
4	177	156
5	210	-205
6	56	52
7	159	166
8	134	-135
9	124	123
10	189	-188
11	14	-1
12	0	0
13	0	-17

-7,4,L

1	36	47
2	0	-4
3	55	57
4	36	29
5	176	174
6	57	53
7	11	-18
8	10	-9
9	5	18
10	90	-76
11	32	-22
12	88	91
13	50	-44

-7,5,L

1	55	62
2	161	-179
3	43	-41
4	149	154
5	92	99
6	162	166
7	271	-275
8	131	-134
9	79	80
10	155	-171
11	30	17
12	0	-6
13	35	17

-7,6,L

1	86	90
2	60	-66
3	0	7
4	165	169
5	155	-146
6	16	3
7	137	-133

-7,6,L

8	63	-68
9	39	-38
10	89	-100
11	52	-56
12	44	-23

-7,7,L

1	11	-16
2	122	-120
3	23	-26
4	213	205
5	120	127
6	154	157
7	0	-16
8	39	28
9	169	-172
10	20	17
11	38	-27
12	20	10

-7,8,L

1	116	110
2	132	-125
3	26	-37
4	246	255
5	59	-61
6	36	42
7	110	-106
8	135	-141
9	78	-85
10	0	-6
11	25	-27
12	40	-10

-7,9,L

1	112	111
2	125	-132
3	75	-78
4	175	181
5	26	-21
6	51	-46
7	28	20
8	162	176
9	30	29
10	60	56
11	0	2
12	32	30

-7,10,L

1	45	46
2	32	-43
3	78	-76
4	173	180
5	9	-17
6	10	11
7	179	-186
8	118	-118
9	59	54
10	0	17
11	26	22
12	65	65

-7,11,L

1	130	-135
2	183	-188
3	186	-189
4	23	0
5	107	-106
6	126	-119
7	64	61
8	70	82
9	99	103
10	92	98
11	35	41
12	14	-26

-7,12,L

1	132	-142
2	34	-26
3	0	-10
4	70	54
5	2	-12
6	24	-10
7	132	-120
8	0	-9
9	135	140
10	63	-66
11	0	-3
12	24	-15

-7,13,L

1	121	-115
2	40	-45
3	40	-37
4	22	16
5	55	-69
6	191	-199
7	43	50
8	14	-5
9	80	83
10	72	82
11	44	42
12	13	-10

-7,14,L

1	50	-51
2	20	35
3	12	12
4	116	120
5	0	11
6	80	-85
7	24	20
8	37	-41
9	127	136
10	0	-16
11	9	-20

-7,15,L

1	40	26
2	12	-5
3	67	50
4	47	53
5	84	-90
6	153	-161
7	74	82
8	15	20
9	25	14
10	10	-19
11	37	35

-7,16,L

1	79	-74
2	54	67
3	76	-73
4	0	-3
5	115	116
6	0	22
7	59	60
8	33	-41
9	45	46
10	0	-5
11	0	-8

-7,17,L

1	25	31
2	66	59
3	72	60
4	10	-19
5	127	-123
6	50	-41
7	64	73
8	20	-14
9	10	2
10	11	20
11	32	-33

-7,18,L

1	19	-15
2	0	9
3	22	-16
4	26	-16
5	99	93
6	0	-0
7	51	-56
8	42	43
9	37	24
10	20	-21

-7,19,L

1	21	7
2	81	00
3	42	30
4	40	46
5	74	-75
6	50	-57
7	30	-19
8	0	6
9	31	22
10	21	4

-7,20,L

1	5	2
2	0	-15
3	79	70
4	25	-30
5	24	33
6	60	54
7	46	-56
8	32	23
9	0	-10
10	6	-5

-7,21,L

1	35	-30
2	10	-20
3	0	41
4	30	32
5	37	-36
6	20	3
7	5	-11
8	4	-20
9	20	-12

-7,22,L

1	33	37
2	30	21
3	6	-25
4	54	-47
5	27	20

-7,22,L

6	75	93
7	0	-11
8	0	8
9	0	-4

-7,23,L

1	17	19
2	29	2
3	0	-10
4	0	-8
5	49	-45
6	0	10
7	33	17
8	45	-46

-7,24,L

1	12	19
2	15	6
3	0	-9
4	19	5
5	53	66
6	0	7
7	0	-6
8	6	-2

-7,25,L

1	15	6
2	0	-7
3	48	50
4	43	49
5	75	-69
6	61	56
7	35	31

-7,26,L

1	0	-11
2	35	24
3	17	9
4	22	-33
5	0	10
6	9	-12

-7,27,L

3	20	34
4	15	-14
5	29	41

-6,0,L

2	131	129
4	189	-191
6	187	182
8	224	-237
10	30	-16
12	75	75

-6,1,L

1	102	116
2	45	36
3	144	-147
4	105	105
5	134	-122
6	344	-356
7	37	41
8	22	22
9	37	27
10	69	63
11	67	73
12	32	-15
13	63	71

-6,2,L

1	125	-124
2	69	-74
3	338	-317
4	213	-204
5	150	-156
6	87	-89
7	14	8
8	23	-22
9	70	79
10	26	-30
11	105	119
12	50	54
13	61	63

-6,3,L

1	196	214
2	17	-8
3	250	-246
4	186	187
5	123	-117
6	190	-200
7	4	-10
8	292	-290
9	121	-126
10	65	60
11	25	-32
12	24	-14
13	34	25

-6,4,L

1	83	-80
2	40	42
3	233	-223
4	141	-145
5	123	126
6	83	80
7	132	-137
8	30	-43
9	175	182
10	50	40
11	41	50
12	30	0
13	15	13

-6,5,L

1	84	-76
2	29	12
3	90	93
4	80	73
5	104	100
6	161	161
7	39	-50
8	341	-331
9	116	-125
10	30	30
11	32	-29
12	21	20
13	56	56

-6,6,L

1	33	31
2	87	95
3	97	-109
4	39	35
5	129	120
6	64	73
7	120	-130
8	282	291
9	120	119
10	31	31
11	61	56
12	20	-21
13	30	-21

-6,7,L

1	105	-102
2	56	-50
3	35	45
4	92	90
5	24	12
6	170	160
7	193	203
8	19	22
9	69	72
10	79	76
11	119	-120
12	0	-13

-6,8,L

1	59	56
2	41	40
3	172	-190
4	127	129
5	59	54
6	60	-72
7	80	-70
8	159	162
9	57	-74
10	42	44
11	16	10
12	0	-2

-6,9,L

1	70	-70
2	30	-41
3	54	59
4	116	110
5	102	175
6	104	100
7	107	102
8	101	-114
9	50	-55
10	102	107
11	149	-142
12	54	-45

-6,10,L

1	233	233
2	72	73
3	207	-217
4	129	126
5	100	114
6	122	-121
7	67	-72
8	145	-147
9	21	-16
10	12	27
11	30	-54
12	0	-17

-6,11,L

1	62	-70
2	30	-26
3	126	114
4	169	-175
5	222	210
6	147	140

-6,11,L

7	21	19
8	115	-116
9	30	-29
10	0	8
11	52	-49
12	38	-27

-6,12,L

1	86	86
2	125	123
3	124	-120
4	160	159
5	224	220
6	274	-275
7	77	73
8	29	33
9	0	-8
10	40	-40
11	0	-6
12	53	-52

-6,13,L

1	139	-149
2	100	98
3	154	-144
4	193	-199
5	223	234
6	63	67
7	0	2
8	71	-72
9	92	89
10	16	-35
11	0	-2
12	0	-10

-6,14,L

1	47	-36
2	162	157
3	43	42
4	25	24
5	142	147
6	195	-207
7	24	-29
8	74	-70
9	35	36
10	20	39
11	0	12
12	0	-1

-6,15,L

1	84	-87
2	76	84
3	173	-187
4	76	-73
5	0	-9
6	0	7
7	20	14
8	0	-5
9	51	49
10	35	23
11	30	29

-6,16,L

1	61	53
2	163	-170
3	75	-89
4	32	-39
5	15	-33
6	136	-141
7	100	-103
8	0	-25
9	0	26
10	72	70
11	19	-2

-6,17,L

1	15	-7
2	0	-12
3	20	7
4	47	-62
5	19	-20
6	12	-15
7	30	-39
8	49	42
9	20	21
10	64	50
11	0	-2

-6,18,L

1	20	7
2	130	-139
3	29	19
4	55	-39
5	24	35
6	56	-60
7	114	-127
8	32	49
9	62	-54
10	85	82
11	36	20

-6,19,L

1	84	82
2	22	13
3	10	-6
4	11	-25
5	74	76
6	53	49
7	97	-103
8	30	31
9	0	0
10	30	32

-6,20,L

1	17	-17
2	15	0
3	42	50
4	0	-2
5	56	67
6	85	-80
7	16	11
8	73	81
9	0	-3
10	40	-20

-6,21,L

1	4	-9
2	35	-36
3	0	21
4	45	-50
5	74	-60
6	24	36
7	11	-13
8	30	47
9	30	-40
10	20	24

-6,22,L

1	52	53
2	43	35
3	45	47
4	19	10
5	0	13
6	70	73
7	0	20
8	10	0
9	21	3

-6,23,L

1	36	-20
2	0	-3
3	24	6
4	27	-19
5	44	-34
6	42	-55
7	30	14
8	14	-13
9	54	30

-6,24,L

1	0	8
2	19	11
3	0	-5
4	102	100
5	0	23
6	70	69
7	0	-6
8	30	-30

-6,25,L

1	24	-21
2	50	-50
3	23	9
4	42	-56
5	54	50
6	24	3
7	0	8
8	31	-25

-6,26,L

1	0	6
2	29	-11
3	36	-45
4	55	56
5	55	-54
6	23	7
7	39	39

-6,27,L

1	20	-33
2	24	7
3	22	10
4	11	14
5	43	40
6	22	-7
7	19	19

-6,28,L

1	9	2
2	17	13
3	0	-5
4	75	-96
5	0	-11
6	36	21

-6,29,L

3	16	4

-6,29,L

4	78	88

-5,0,L

2	585	-567
4	124	125
6	146	151
8	29	37
10	227	-254
12	49	-31

-5,1,L

1	249	-268
2	255	250
3	32	-24
4	2	-24
5	88	-83
6	204	-210
7	80	-81
8	123	-122
9	233	233
10	39	-29
11	23	33
12	19	4
13	0	-11

-5,2,L

1	133	128
2	93	83
3	36	40
4	239	218
5	0	6
6	20	-18
7	150	142
8	36	34
9	71	-85
10	55	-57
11	14	-12
12	51	-62
13	0	10

-5,3,L

1	188	192
2	250	246
3	283	-274
4	25	16
5	61	-45
6	171	-165
7	97	101
8	284	-281
9	93	101
10	25	-23
11	0	-10
12	30	15
13	51	41

-5,4,L

1	61	56
2	18	20
3	27	20
4	264	265
5	154	-161
6	93	89
7	182	189
8	46	48
9	62	-66
10	23	-18
11	31	21
12	28	-29
13	26	-19

-5,5,L

1	114	116
2	205	222
3	66	60
4	1	4
5	34	31
6	75	-71
7	105	-105
8	117	-125
9	83	-95
10	71	80
11	12	-9
12	51	50
13	33	24

-5,6,L

1	48	49
3	47	43
4	10	-3
5	275	-269
6	60	-70
7	210	-210
8	56	63
9	22	-23
10	0	7
11	60	60
12	10	24

-5,7,L

1	216	212
2	215	215
3	300	299
4	290	-281
5	254	230
6	249	-249
7	520	-529
8	17	7
9	36	-15
10	41	49
11	37	-27
12	31	20

-5,8,L

1	106	-112
2	95	-104
3	0	17
4	360	-342
5	104	-101
6	47	-36
7	79	83
8	24	15
9	150	-160
10	84	85
11	7	10
12	0	-14

-5,9,L

1	14	-4
2	101	-95
3	261	254
4	130	130
5	0	17
6	60	-59
7	0	0
8	115	-110
9	110	-112
10	37	42
11	2	-4
12	0	-8

-5,10,L

1	79	-80
2	96	112
3	129	131
4	127	-135
5	61	60
6	26	-33
7	303	301
8	30	41
9	10	16
10	27	-1
11	22	6
12	0	-10

-5,11,L

1	40	44
2	33	42
3	84	-81
4	20	31
5	5	-6
6	90	96
7	0	27
8	62	-50
9	110	132
10	51	51
11	34	22
12	15	-23

-5,12,L

1	95	-95
2	89	85
3	115	110
4	5	-3
5	11	-3
6	90	-92
7	94	97
8	140	153
9	140	159
10	10	14
11	31	27
12	49	-57

-5,13,L

1	283	-270
2	0	7
3	61	-49
4	126	-120
5	27	-14
6	171	163
7	1	-21
8	70	71
9	54	71
10	109	-102
11	50	43
12	36	-33

-5,14,L

1	266	-266
2	163	173
3	19	10
4	155	-150
5	47	50
6	73	69
7	144	150
8	62	50
9	90	-107
10	26	13
11	0	14
12	101	-95

-5,15,L

2	45	26
3	159	164
4	108	-111
5	0	-23
6	175	180
7	90	-92
8	75	68
9	69	-70
10	39	-37
11	28	-18

-5,16,L

1	248	261
2	31	34
3	36	-29
4	79	-75
5	61	-63
6	81	85
7	186	185
8	0	-1
9	89	-89
10	42	-42
11	8	11

-5,17,L

1	212	221
2	113	110
3	185	184
4	117	-125
5	0	-9
6	236	240
7	0	-16
8	35	38
9	23	-26
10	0	13
11	61	-70

-5,18,L

1	168	184
2	122	-138
3	28	37
4	113	-113
5	97	-107
6	97	96
7	87	-92
8	16	-8
9	56	-55
10	42	39
11	36	20

-5,19,L

1	0	10
2	0	0
3	59	70
4	107	-109
5	95	96
6	133	143
7	30	23
8	0	-14
9	44	-55
10	54	-56

-5,20,L

1	101	98
2	74	-81
3	55	-52
4	29	-40
5	239	-242
6	72	75
7	88	-88
8	49	-52
9	18	-19
10	47	60

-5,21,L

1	60	63
2	82	76
3	57	-69
4	99	-112
5	120	122
6	94	-101
7	48	-52
8	31	-33
9	1	-21
10	14	-4

-5,22,L

1	81	89
2	82	-87
3	67	-71
4	0	22
5	0	-12
6	114	121
7	51	-47
8	67	-83
9	0	-6

-5,23,L

1	44	-30
2	29	31
3	43	-64
4	16	-7
5	115	-124
6	0	-1
7	10	10
8	68	-77
9	0	12

-5,24,L

1	0	-5
2	0	5
3	0	15
4	33	34
5	136	143
6	72	80
7	0	-9
8	71	-89
9	19	20

-5,25,L

1	33	-39
2	17	-9
3	97	-103
4	30	37
5	41	-41
6	25	-2
7	0	-11
8	0	-17

-5,26,L

1	0	2
2	24	7
3	56	57
4	44	34
5	0	-1
6	23	14
7	0	9
8	15	8

-5,27,L

1	33	-25
2	31	-5
3	17	10
4	75	85
5	0	2
6	33	-21
7	0	10

-5,28,L

1	46	-43
2	0	8
3	12	-45
4	24	-20
5	61	60
6	0	-11

-5,29,L

1	21	25
2	27	-19
3	72	73
4	35	17
5	0	-13
6	33	22

-5,30,L

1	0	-9
2	28	-14
3	67	-77
4	36	-22

-4,0,L

2	31	-30
4	244	233
6	145	149
8	223	-235
10	17	2
12	54	-35

-4,1,L

1	437	-452
2	58	58
3	707	-667
4	39	46
5	425	406
6	106	-87
7	31	35
8	48	51
9	219	223
10	29	40
11	0	-2
12	15	-5
13	74	-62

-4,2,L

1	389	-315
2	57	-50
3	478	452
4	224	217
5	267	-272
6	267	254
7	94	-94
8	280	-292
9	120	122
10	169	179
11	20	13
12	25	-29

-4,3,L

2	194	-204
3	279	-262
4	139	-135
5	131	114
6	360	-343
7	25	27
8	166	171
9	48	43
10	106	99
11	40	36
12	0	-4

-4,4,L

1	75	-79
2	487	-481
3	188	-178
4	253	240
5	205	182
6	67	-57
7	9	-21
8	119	-130
9	64	67
10	172	167
11	90	-101
12	11	-6

-4,5,L

2	237	-229
3	63	-53
4	169	-172
5	146	-147
6	319	-328
7	40	-44
8	112	111
9	63	73
10	120	120
11	107	-111
12	0	-5

-4,6,L

1	26	-6
2	155	156
3	403	368
4	134	-131
5	216	217
6	16	-11
7	39	-38
8	142	-136
9	66	-69
10	20	22
11	80	-71
12	6	1

-4,7,L

1	132	135
2	342	329
3	215	189
4	197	182
5	172	167
6	218	-216
7	124	-126
8	187	190
9	39	41
10	38	48
11	19	-36
12	26	-32

-4,8,L

1	0	-10
2	507	484
3	279	262
4	317	-316
5	101	-98
6	100	-105
7	31	33
8	66	61
9	0	6
10	54	-48
11	69	-70
12	21	7

-4,9,L

1	292	288
2	125	131
3	297	294
4	144	143
5	58	-52
6	12	-19
7	34	24
8	232	233
9	47	-45
10	60	-63
11	34	29
12	40	-36

-4,10,L

1	69	-69
2	286	282
3	217	-203
4	60	61
5	96	-103
6	69	-63
7	27	28
8	90	-97
9	23	24
10	54	-52
11	11	-24
12	0	0

-4,11,L

1	333	331
2	123	113
3	19	11
4	35	-28
5	196	-204
6	13	-16
7	110	-112
8	116	-115
9	75	-65
10	58	-59
11	30	-29
12	37	35

-4,12,L

1	50	-47
2	111	100
3	202	213
4	60	64
5	64	-60
6	82	85
7	0	-2
8	151	-156
9	0	3
10	52	-62
11	45	49
12	31	-38

-4,13,L

1	94	90
2	0	5
3	250	-259
4	63	-57
5	246	-239
6	36	-38
7	55	-66
8	56	-41
9	29	-28
10	96	-106
11	38	41
12	46	40

-4,14,L

1	15	14
2	21	24
3	26	-19
4	86	86
5	63	60
6	147	152
7	109	116
8	195	200
9	24	-35
10	87	-90
11	19	-26

-4,15,L

1	141	-140
2	19	20
3	162	-149
4	29	27
5	12	-4
6	155	-156
7	110	112
8	43	45
9	7	-19
10	3	12
11	72	72

-4,16,L

1	34	30
2	60	-69
3	55	52
4	31	-34
5	116	-111
6	296	295
7	94	-96
8	76	79
9	27	-0
10	49	63
11	25	10

-4,17,L

1	0	13
2	149	-141
3	64	-55
4	4	-2
5	34	-23
6	59	53
7	123	130
8	34	-37
9	53	44
10	52	62
11	0	-11

-4,18,L

1	126	-127
2	302	-301
3	36	41
4	27	13
5	112	-112
6	132	-136

-4,18,L

7	0	-16
8	66	65
9	19	21
10	22	37
11	26	15

-4,19,L

1	40	-38
2	151	-164
3	63	70
4	0	21
5	32	-26
6	217	231
7	89	94
8	13	-5
9	20	-16
10	10	-44

-4,20,L

1	55	-44
2	27	-29
3	27	34
4	10	-25
5	0	-10
6	103	-120
7	51	46
8	39	-29
9	15	23
10	26	-42

-4,21,L

1	0	27
2	237	250
3	0	36
4	161	162
5	33	-34
6	43	-41
7	110	116
8	23	-19
9	10	25
10	19	-24

-4,22,L

1	80	-81
2	163	176
3	39	-37
4	63	67
5	16	-19
6	32	-34
7	83	79
8	39	-49
9	6	-24

-4,23,L

1	46	50
2	66	80
3	1	6
4	7	-32
5	105	-113
6	21	26
7	40	48
8	17	-34
9	30	25

-4,24,L

1	70	-80
2	53	49
3	44	-47
4	197	209
5	62	-62
6	70	-90
7	64	73
8	49	-50
9	0	-2

-4,25,L

1	21	-6
2	32	20
3	23	4
4	100	-111
5	32	-41
6	0	-2
7	46	-49
8	27	-24

-4,26,L

1	0	10
2	54	73
3	50	52
4	0	7
5	0	-9
6	25	-27
7	17	14
8	20	-20

-4,27,L

1	32	22
2	0	20
3	0	-15
4	36	-43
5	5	-20
6	14	-35
7	17	-6

-4,28,L

1	0	4
2	0	-21
3	24	21
4	24	-27
5	0	20
6	0	-11
7	0	34

-4,29,L

1	0	13
2	19	40
3	1	9
4	21	-33
5	14	12
6	31	-15

-4,30,L

1	27	21
2	13	-36
3	16	13
4	10	-20
5	24	7

-4,31,L

1	15	-19
2	0	14
3	4	3
4	10	9

-3,0,L

2	355	337
4	199	197
6	464	-451
8	95	95
10	130	127
12	0	-23

-3,1,L

1	424	-433
2	224	-226
3	442	433
4	237	-240
5	171	167
6	60	-75
7	95	89
8	63	72
9	129	-126
10	72	-71
11	7	-7
12	42	27

-3,2,L

2	317	305
3	305	299
4	356	-335
5	447	435
6	19	-21
7	160	151
8	0	21
9	34	-39
10	46	50
11	0	20
12	0	-1

-3,3,L

1	219	-223
2	23	22
3	209	198
4	832	-809
5	272	-259
6	0	2
7	230	233
8	132	133
9	162	-179
10	0	0
11	0	7
12	15	-25

-3,4,L

1	15	-5
2	340	344
3	225	-223
4	25	14
5	80	-85
6	77	69
7	202	202
8	53	-54
9	29	20
10	43	57
11	30	-16
12	34	12

-3,5,L

1	211	210
2	35	-36
3	100	93
4	685	-646
5	80	67
6	139	127
7	4	10
8	156	154

-3,5,L

9	102	-110
10	80	83
11	0	6
12	35	-35

-3,6,L

1	143	139
2	169	-155
3	198	-207
4	74	-73
5	399	-395
6	186	95
7	73	79
8	17	-16
9	9	0
10	61	52
11	0	20
12	18	-1

-3,7,L

1	146	-126
2	394	-387
3	30	21
4	104	113
5	125	113
6	98	100
7	37	-35
8	145	143
9	132	-124
10	47	43
11	94	97
12	30	26

-3,8,L

1	221	-194
2	65	67
3	91	-84
4	605	-592
5	133	-127
6	34	-40
7	117	-123
8	46	-52
9	36	-32
10	4	-4
11	54	55
12	0	10

-3,9,L

1	17	9
2	280	272
3	490	-475
4	212	-219
5	153	141
6	44	50
7	0	5
8	79	82
9	0	5
10	30	39
11	77	69
12	70	-77

-3,10,L

1	272	-248
2	89	74
3	62	71
4	229	-223
5	10	-3
6	82	87
7	224	-232
8	67	-66
9	77	-79
10	41	-30
11	40	44
12	14	0

-3,11,L

1	317	-300
2	264	266
3	214	-214
4	406	303
5	74	-81
6	103	103
7	375	373
8	105	-100
9	3	10
10	56	-46
11	22	20
12	59	-54

-3,12,L

1	75	-60
2	122	107
3	311	299
4	95	89
5	12	3
6	245	254
7	142	-145
8	30	46
9	2	1
10	13	-11
11	0	11

-3,13,L

1	53	77
2	70	-61
3	26	10
4	390	300
5	37	32
6	31	22
7	200	-202
8	02	-93
9	107	106
10	23	-21
11	0	10

-3,14,L

1	26	30
2	05	73
3	170	172
4	40	-45
5	63	54
6	90	100
7	126	140
8	96	90
9	17	20
10	30	-44
11	22	-15

-3,15,L

1	06	-79
2	01	-04
3	43	-37
4	30	25
5	33	-29
6	65	-55
7	172	-105
8	00	-07
9	05	-79
10	37	41
11	27	-26

-3,16,L

1	74	-72
2	07	96
3	203	201
4	34	-32
5	353	340
6	03	-04
7	21	9
8	21	4
9	111	-115
10	0	-7
11	9	-15

-3,17,L

1	107	99
2	216	-219
3	0	6
4	10	-24
5	27	-34
6	31	-27
7	64	50
8	123	-125
9	54	-62
10	19	-16
11	40	-47

-3,18,L

1	110	113
2	105	103
3	19	-10
4	03	04
5	64	-65
6	145	-140
7	25	27
8	62	-52
9	42	40
10	21	35

-3,19,L

1	49	59
2	172	-169
3	30	20
4	03	-05
5	256	260
6	0	-0
7	65	-70
8	53	51
9	05	92
10	14	0

-3,20,L

1	203	-212
2	22	-15
3	107	-110
4	24	13
5	100	-101
6	36	-43
7	41	53
8	13	-13
9	75	75
10	16	-6

-3,21,L

1	226	-229
2	56	-51
3	61	63
4	90	89
5	23	36

-3,21,L

6	44	-37
7	2	0
8	53	46
9	38	29
10	20	14

-3,22,L

1	162	-178
2	17	-2
3	186	-192
4	0	-2
5	8	-14
6	126	-132
7	6	7
8	6	2
9	30	18

-3,23,L

1	29	11
2	54	-56
3	139	-156
4	6	25
5	23	13
6	50	-49
7	15	-16
8	46	53
9	18	21

-3,24,L

1	0	20
2	0	-15
3	6	1
4	54	54
5	9	-25
6	56	-60
7	0	0
8	56	63
9	0	16

-3,25,L

1	49	-49
2	0	13
3	2	7
4	27	18
5	34	35
6	32	-24
7	0	5
8	22	7

-3,26,L

1	42	-40
2	0	-8
3	171	192
4	0	20
5	36	42
6	0	-19
7	0	-16
8	73	70

-3,27,L

1	23	-18
2	41	40
3	105	116
4	0	-8
5	0	14
6	48	-59
7	26	-30

-3,28,L

1	55	48
2	34	-30
3	36	41
4	6	-15
5	17	30
6	35	-44
7	0	14

-3,29,L

1	19	14
2	31	13
3	52	62
4	10	-13
5	0	11
6	33	-23

-3,30,L

1	33	32
2	20	-29
3	20	11
4	1	-9
5	0	-7

-3,31,L

1	0	-8
2	41	39
3	0	21
4	0	-8

-3,32,L

1	0	20
2	0	-20
3	20	17

-2,0,L

2	980	964
4	285	291
6	60	44
8	46	-35
10	123	-125
12	0	-16

-2,1,L

1	478	472
2	352	333
3	317	313
4	38	48
5	369	364
6	144	-137
7	190	180
8	32	31
9	51	-59
10	61	-56
11	47	-45
12	21	-5

-2,2,L

2	316	316
3	629	-612
4	133	136
5	90	80
6	142	-139
7	69	76
8	136	145
9	42	41
10	115	-114
11	17	27
12	0	-5

-2,3,L

2	138	136
3	1049	1040
4	140	-142
5	524	-511
6	132	-134
7	81	-81
8	54	44
9	77	-74
10	76	-74
11	0	-8
12	0	-9

-2,4,L

1	90	-90
2	64	-73
3	115	107
4	173	-176
5	209	204
6	183	180
7	75	79
8	153	155
9	0	9
10	0	-5
11	78	80
12	0	-5

-2,5,L

1	342	-326
2	496	-470
3	31	-27
4	60	-66
5	186	-184
6	83	87
7	157	-154
8	95	-97
9	0	3
10	77	-82
11	0	-3
12	31	26

-2,6,L

1	247	244
2	427	-430
3	113	120
4	130	-127
5	99	103
6	10	9
7	53	45
8	277	290
9	79	-74
10	32	-23
11	35	-17
12	20	15

-2,7,L

1	57	-55
2	402	-402
3	232	-252
4	104	89
5	415	-416
6	200	199
7	96	92
8	42	-38
9	114	116
10	146	-144
11	52	40
12	14	16

-2,8,L

1	147	142
2	54	-46
3	294	-285
4	69	-53
5	220	-220
6	4	5
7	22	21
8	12	-15
9	73	-79
10	48	-45
11	16	17
12	29	36

-2,9,L

1	172	-162
2	490	487
3	89	57
4	165	164
5	257	-246
6	57	49
7	92	103
8	252	263
9	54	50
10	89	-87
11	71	55

-2,10,L

1	195	181
2	294	-299
3	306	-290
4	168	-167
5	130	-133
6	50	-53
7	0	11
8	150	-170
9	56	-46
10	20	-13
11	102	96

-2,11,L

1	85	-75
2	15	17
3	87	-77
4	126	120
5	76	-82
6	239	236
7	31	-26
8	32	39
9	62	64
10	33	-40
11	34	32

-2,12,L

1	136	140
2	458	-444
3	260	-243
4	90	-102
5	32	-40
6	123	-125
7	86	89
8	77	-80
9	37	-39
10	0	-19
11	16	-1

-2,13,L

1	165	-166
2	271	-267
3	247	233
4	45	-47
5	186	189
6	143	-141
7	86	-85
8	113	-102
9	19	-22
10	0	13
11	45	51

-2,14,L

1	65	72
2	89	-87
3	112	133
4	77	-72
5	199	-194
6	389	326
7	0	-6
8	162	-150
9	44	31
10	20	-13
11	0	-1

-2,15,L

1	146	120
2	216	-215
3	124	124
4	31	-20
5	131	120
6	316	-324
7	70	77
8	46	55
9	67	-64
10	30	13
11	0	-5

-2,16,L

1	147	-140
2	93	-87
3	32	41
4	260	274
5	181	189
6	62	60
7	72	77
8	35	24
9	0	13
10	0	5
11	29	-13

-2,17,L

1	87	91
2	94	-84
3	110	103
4	70	79
5	79	80
6	0	-5
7	9	21
8	20	-9
9	59	-51
10	51	52

-2,18,L

1	96	80
2	34	29
3	49	47
4	95	97
5	102	107
6	60	55
7	5	24
8	43	-54
9	60	54
10	43	46

-2,19,L

1	186	-186
2	76	-71
3	105	111
4	159	161
5	23	-11
6	70	-82
7	39	-23
8	40	-30
9	30	34
10	23	31

-2,20,L

1	75	-76
2	26	-14
3	47	46
4	80	-99
5	4	-13
6	41	51
7	41	-29
8	23	25
9	43	-42
10	43	-39

-2,21,L

1	32	-52
2	50	-54
3	10	-6
4	115	110
5	20	-27
6	34	32
7	0	-14
8	23	11
9	39	16

-2,22,L

1	0	11
2	175	180
3	0	-2
4	0	5
5	12	1
6	64	-53
7	47	-51
8	17	14
9	35	-29

-2,23,L

1	95	101
2	145	152
3	33	-35
4	22	-19
5	42	-45
6	45	38
7	12	-19
8	36	32
9	31	-30

-2,24,L

1	110	120
2	0	-8
3	22	-19
4	0	3
5	11	-36
6	6	-16
7	26	-9
8	4	11

-2,25,L

2	93	-96
3	45	-45
4	74	-82
5	42	-40
6	11	19
7	75	-63
8	0	16

-2,26,L

1	39	-44
2	177	-196
3	19	13
4	55	-49
5	22	22
6	0	7
7	0	12
8	42	25

-2,27,L

1	46	49
2	20	-27
3	38	-42
4	80	-91
5	0	23
6	35	-42
7	61	-60

-2,28,L

1	0	-1
2	31	-40
3	0	10
4	90	-100
5	0	16
6	51	46
7	1	-16

-2,29,L

1	50	56
2	66	70
3	27	-29
4	27	-10
5	35	42
6	19	-13

-2,30,L

1	25	-26
2	73	-82
3	42	-29
4	57	60
5	0	-7

-2,31,L

1	26	40
2	30	9
3	14	-2
4	74	69
5	29	39

-2,32,L

1	46	-57
2	0	-3
3	0	5

-2,33,L

1	22	34

-1,0,L

2	323	-321
4	469	-471
6	122	-130
8	19	-15
10	27	-37

-1,1,L

1	1272	-1310
2	20	6
3	77	74
4	262	252
5	245	-251
6	62	-56
7	111	113
8	22	-23
9	136	140
10	49	-52
11	34	30

-1,2,L

1	342	-349
2	891	901
3	30	-20
4	267	270
5	431	457
6	270	-279
7	127	130
8	0	-7
9	112	-105
10	22	-15
11	36	-25

-1,3,L

1	480	494
2	350	350
3	80	-94
4	121	136
5	20	14
6	121	123
7	101	99
8	52	-52
9	20	5
10	94	-99
11	0	-2

-1,4,L

1	139	143
2	696	684
3	51	-52
4	139	130
5	288	299
6	89	93
7	69	66
8	51	53
9	75	81
10	30	-15
11	10	-25

-1,5,L

1	652	-628
2	116	102
3	173	-170
4	31	-15
5	123	-121
6	430	436
7	7	-3
8	71	-65
9	129	-140
10	65	-79
11	19	-23

-1,6,L

1	327	-313
2	316	-313
3	16	-23
4	213	201
5	197	191
6	73	73
7	139	151
8	5	10
9	84	86
10	57	54
11	41	-42

-1,7,L

1	587	580
2	156	-159
3	17	35
4	65	-31
5	107	-96
6	83	81
7	357	-361
8	39	44
9	34	40
10	31	-35
11	37	-30

-1,8,L

1	30	13
2	844	-830
3	4	7
4	543	514
5	197	197
6	31	30
7	84	-89
8	52	-62
9	29	20
10	20	11
11	0	-5

-1,9,L

1	321	-327
2	210	-215
3	2	24
4	109	-95
5	49	-54
6	289	-284
7	265	270
8	42	-40
9	0	1
10	41	20
11	27	-13

-1,10,L

1	257	255
2	26	-32
3	305	-287
4	171	166
5	52	54
6	47	-34
7	262	-277
8	63	-62
9	53	55
10	0	0
11	30	-6

-1,11,L

1	280	-310

-1,11,L

2	150	-139
3	170	-195
4	120	-117
5	295	290
6	92	-85
7	123	124
8	27	-16
9	87	66
10	42	34
11	33	-35

-1,12,L

1	200	188
2	137	146
3	222	-221
4	152	149
5	273	-266
6	237	-241
7	39	31
8	57	-57
9	60	71
10	10	-6
11	46	-43

-1,13,L

1	231	-239
2	310	290
3	173	159
4	82	79
5	87	84
6	197	-197
7	25	-12
8	49	56
9	49	42
10	39	38
11	36	-42

-1,14,L

1	66	56
2	393	-364
3	213	209
4	143	141
5	38	52
6	182	-189
7	111	-189
8	47	35
9	54	48
10	6	12

-1,15,L

1	264	259
2	218	206
3	142	156
4	98	-93
5	172	-171
6	132	-134
7	0	20
8	56	55
9	18	20
10	32	-15

-1,16,L

1	79	72
2	26	18
3	50	-46
4	63	-52
5	88	90
6	85	-84
7	14	-8
8	39	36
9	14	-17
10	62	54

-1,17,L

1	261	250
2	27	20
3	85	-76
4	91	-92
5	0	-4
6	93	-92
7	28	-31
8	36	27
9	65	-58
10	19	-7

-1,18,L

1	93	96
2	70	69
3	50	-50
4	24	22
5	76	-80
6	41	-44
7	75	69
8	21	2
9	32	-25
10	45	-36

-1,19,L

1	81	87
2	144	146
3	135	-120
4	157	163
5	21	-20
6	21	-18
7	8	-4
8	20	20
9	0	-27

-1,20,L

1	29	44
2	96	92
3	0	-23
4	20	-20
5	70	-73
6	32	39
7	22	10
8	0	15
9	43	31

-1,21,L

1	37	39
2	25	-24
3	153	-163
4	50	60
5	40	52
6	111	105
7	25	5
8	121	121
9	0	24

-1,22,L

1	121	-125
2	100	100
3	20	34
4	41	-55
5	53	50
6	82	81
7	20	-27
8	0	19
9	27	-10

-1,23,L

1	60	-61
2	114	-114
3	102	-109
4	54	53
5	12	-11
6	27	33
7	95	92
8	15	17

-1,24,L

1	0	15
2	9	10
3	46	50
4	30	-29
5	65	63
6	20	10
7	20	-31
8	0	-3

-1,25,L

1	94	100
2	105	-115
3	144	-140
4	25	-16
5	26	25
6	0	-32
7	42	36
8	30	-10

-1,26,L

1	53	54
2	49	51
3	54	59
4	29	-30
5	27	17
6	49	40
7	16	0

-1,27,L

1	0	6
2	72	-71
3	62	70
4	0	-4
5	0	7
6	14	-0
7	7	11

-1,28,L

1	47	-64
2	120	145
3	0	14
4	20	-10
5	6	24
6	0	7

-1,29,L

1	42	34
2	24	-2
3	27	11
4	29	-10
5	32	-25
6	0	-10

-1,30,L

2	29	-10
3	83	-94
4	22	8
5	0	-14

-1,31,L

1	26	45
2	0	1
3	71	-83
4	0	-9

-1,32,L

1	17	-13
2	0	-2
3	34	-35

-1,33,L

1	0	-6
2	21	-4

0,0,L

2	230	-252
4	252	-262
6	199	-215
8	114	-114
10	152	-166

0,1,L

1	23	-11
2	0	-21
3	271	-309
4	227	253
5	267	299
6	19	10
7	56	-61
8	114	114
9	29	4
10	17	0
11	73	71

0,2,L

0	935	886
1	329	-323
2	286	301
3	115	-122
4	95	-100
5	50	-64
6	36	-46
7	56	-52
8	198	-212
9	46	46
10	33	-25
11	15	15

0,3,L

1	80	-94
2	330	-350
3	365	-357
4	334	354
5	142	153
6	4	-20
7	57	-53
8	31	-26
9	66	-72
10	77	76
11	0	30

0,4,L

0	422	-395
1	255	-257
2	977	-982
3	383	393
4	36	36
5	135	-121
6	120	-127
7	199	-209
8	201	204
9	0	-1
10	53	45
11	17	22

0,5,L

1	490	472
2	1136	-1137
3	27	-19
4	44	-36
5	10	22
6	1	-4
7	21	-21
8	215	-226
9	7	-12
10	81	79
11	0	-6

0,6,L

0	169	148
1	398	-394
2	769	-769
3	197	197
4	63	59
5	188	189
6	161	164
7	129	-133
8	159	150
9	0	-6
10	42	26
11	29	-11

0,7,L

1	619	-619
2	148	-151
3	476	452
4	49	51
5	331	327
6	161	-157
7	64	-66
8	26	-13
9	12	-16
10	27	35
11	59	-44

0,8,L

0	540	-535
1	284	-280
2	145	-124
3	358	333
4	87	81
5	142	140
6	121	119
7	27	10
8	17	22
9	31	35
10	0	4
11	5	3

0,9,L

1	420	-421
2	102	94
3	77	-60
4	202	194
5	57	-54
6	92	94
7	93	92
8	46	-39
9	57	41
10	3	4
11	52	-30

0,10,L

0	417	-432
1	214	211
2	0	-11
3	180	157
4	145	130
5	65	-55
6	213	-216
7	106	103
8	112	107
9	0	5
10	10	19

0,11,L

1	384	-361
2	167	-165
3	29	42
4	45	-49
5	23	20
6	109	104
7	5	-6
8	40	-45
9	23	10
10	32	30

0,12,L

0	296	-314
1	250	245
2	277	272
3	103	-97
4	102	104
5	0	7
6	36	-26
7	30	-33
8	54	-51
9	26	17
10	49	35

0,13,L

1	101	84
2	60	-64
3	60	-70
4	154	-145
5	01	66
6	61	-61
7	40	-49
8	50	39
9	0	10
10	50	36

0,14,L

0	436	441
1	316	-297
2	50	60
3	0	-14
4	79	-70
5	66	59
6	52	-44
7	30	-27

0,14,L

8	33	-28
9	19	-13
10	10	3

0,15,L

1	219	203
2	159	155
3	60	56
4	116	-106
5	97	-93
6	21	-12
7	51	-50
8	40	49
9	50	-45
10	14	11

0,16,L

0	73	-34
1	42	46
2	150	154
3	100	-100
4	171	-175
5	40	-28
6	32	28
7	0	-9
8	19	1
9	49	41
10	31	26

0,17,L

1	82	79
2	140	132
3	163	172
4	63	62
5	46	-34
6	0	-13
7	79	-68
8	1	12
9	46	-37

0,18,L

0	60	-67
1	73	82
2	0	7
3	156	-149
4	27	-37
5	55	59
6	23	-11
7	0	-15
8	87	77
9	10	14

0,19,L

1	60	71
2	30	33
3	24	39
4	149	155
5	20	3
6	50	57
7	59	-41
8	62	-50
9	20	14

0,20,L

0	0	-17
1	30	-26
2	85	91
3	9	-4
4	140	-141
5	24	-13
6	20	24
7	73	-73
8	20	0
9	21	20

0,21,L

1	104	-90
2	86	84
3	50	54
4	0	22
5	30	-32
6	0	4
7	7	15
8	0	-4

0,22,L

0	80	76
1	47	42
2	69	70
3	104	-115
4	105	-105
5	0	0
6	1	6
7	52	-53
8	35	7

0,23,L

1	124	-137
2	39	34
3	94	99
4	60	-74
5	30	30
6	19	22
7	10	16
8	0	-5

0,24,L

0	17	-3
1	127	130
2	72	70
3	56	-63
4	11	6
5	30	46
6	20	-11
7	0	0
8	0	5

0,25,L

1	56	-70
2	54	-63
3	1	6
4	25	-30
5	36	37
6	0	4
7	7	20

0,26,L

0	34	-15
1	84	89
2	26	10
3	46	49
4	46	-60
5	0	0
6	0	25
7	7	27

0,27,L

1	109	-127
2	137	-130
3	27	-19
4	30	-26
5	0	19
6	33	29

0,28,L

0	23	1
1	0	34
2	33	-44
3	31	-33
4	0	-1
5	21	21
6	0	9

0,29,L

1	32	-37
2	32	36
3	0	-4
4	0	-17
5	0	6

0,30,L

0	11	-24
1	29	34
2	61	62
3	0	-26
4	2	-12
5	0	-8

0,31,L

1	67	75
2	10	17
3	0	2
4	40	44

0,32,L

0	0	-3
1	6	6
2	0	0
3	0	12

0,33,L

1	0	14
2	14	-17

1,0,L

0	47	70
2	123	137
4	39	-34
6	157	172
8	34	35
10	0	13

1,1,L

0	11	-14
1	50	-53
2	233	-240
3	92	-91
4	215	-240
5	40	50
6	19	-27
7	67	-71
8	32	46
9	166	167
10	13	4

1,2,L

0	121	-126
1	20	23
2	451	-458
3	479	563
4	11	19
5	63	-74
6	142	163
7	192	-214
8	0	-18
9	72	-68
10	29	-31

1,3,L

0	322	-325
1	41	34
2	52	-44
3	121	-126
4	117	115
5	68	72
6	0	3
7	186	184
8	19	-27
9	96	-101
10	29	5

1,4,L

0	69	54
1	1937	1946
2	61	-56
3	344	350
4	137	-149
5	64	-65
6	45	-39
7	60	-65
8	67	-60
9	76	-77
10	5	15

1,5,L

0	51	-43
1	2138	2174
2	738	787
3	52	-56
4	332	324
5	58	60
6	36	31
7	284	-289
8	29	-25
9	33	26
10	0	9

1,6,L

0	212	-206
1	993	1007
2	587	-556
3	55	-52
4	161	-144
5	83	-85
6	143	136
7	24	29
8	28	-24
9	5	-6
10	0	3

1,7,L

0	367	-360
1	57	39
2	289	258
3	199	187
4	30	27
5	24	-24
6	77	-75
7	40	-36
8	31	-38
9	30	-17
10	0	13

1,8,L

0	420	-422
1	504	-493
2	26	-8
3	74	-81
4	31	-30
5	30	33
6	51	46
7	110	-119
8	0	3
9	43	32
10	0	-3

1,9,L

0	32	31
1	401	389
2	696	-564
3	267	-266
4	56	60
5	32	-25
6	80	-65
7	16	-5
8	9	-22
9	0	4
10	21	5

1,10,L

0	95	102
1	59	-46
2	631	606
3	329	-325
4	13	7
5	22	-10
6	113	-105
7	30	12
8	33	-22
9	49	44
10	44	-29

1,11,L

0	22	-3
1	93	-84
2	249	-229
3	261	-264
4	13	-11
5	70	-74
6	130	122
7	100	100
8	17	-14
9	22	-6
10	51	35

1,12,L

0	30	37
1	99	-112
2	0	-2
3	251	-248
4	212	196
5	85	90
6	40	35
7	20	30
8	0	-7
9	0	3
10	40	-39

1,13,L

0	55	-64
1	63	-40
2	19	17
3	7	-9
4	81	-73
5	139	-136
6	122	113
7	27	21
8	36	41
9	70	58

1,14,L

0	243	-245
1	0	2
2	119	117
3	156	-157
4	132	126
5	149	146
6	0	-16
7	40	45
8	50	59
9	47	-40

1,15,L

0	20	-41
1	32	40
2	139	-143
3	91	89
4	119	-113
5	155	-153
6	41	37
7	32	-22
8	40	29
9	0	21

1,16,L

0	216	-217
1	100	100
2	53	-44
3	3	-14
4	4	14
5	152	154
6	30	9
7	0	11
8	67	51
9	40	-34

1,17,L

0	116	106
1	35	-21
2	93	92
3	24	37
4	222	-218
5	33	-37
6	61	53
7	28	-8
8	69	-62
9	13	-23

1,18,L

0	136	142
1	145	151
2	181	-175
3	67	-64
4	60	73
5	40	-41

1,18,L

6	0	2
7	44	37
8	25	-24
9	0	-28

1,19,L

0	242	251
1	68	74
2	193	201
3	4	6
4	111	-125
5	34	39
6	15	26
7	21	-26
8	49	-43

1,20,L

0	169	176
1	26	23
2	166	-178
3	73	-74
4	63	62
5	51	-53
6	0	14
7	8	4
8	44	-34

1,21,L

0	31	36
1	63	-56
2	186	196
3	132	149
4	67	68
5	37	-38
6	7	3
7	0	-6
8	41	-33

1,22,L

0	42	-46
1	31	-28
2	199	-199
3	2	-11
4	0	-4
5	27	22
6	46	44
7	20	-11
8	0	-11

1,23,L

0	40	32
1	51	-58
2	121	127
3	10	12
4	23	-27
5	81	74
6	24	10
7	28	-15

1,24,L

0	0	11
1	30	-23
2	134	-139
3	71	71
4	33	24
5	2	10
6	0	15
7	0	10

1,25,L

0	88	-94
1	38	-51
2	46	-46
3	40	38
4	14	15
5	0	3
6	36	-22
7	0	4

1,26,L

0	36	43
1	5	-9
2	0	7
3	36	39
4	20	22
5	20	-17
6	21	-22

1,27,L

0	91	-102
1	27	10
2	45	-52
3	45	45
4	23	-1
5	35	-35
6	17	-0

1,28,L

0	46	-42
1	24	-20
2	0	2
3	23	32
4	24	17
5	0	-11

1,29,L

0	117	-129
1	0	-11
2	37	32
3	28	31
4	21	12
5	51	-46

1,30,L

0	34	-52
1	35	-28
2	27	25
3	0	-8
4	0	6

1,31,L

0	66	-76
1	30	7
2	20	-25
3	0	-9

1,32,L

0	36	-52
1	0	9
2	38	-5

1,33,L

0	40	-38
1	0	7

2,0,L

0	369	-407
2	61	-47
4	72	-87
6	12	16
8	170	-176

2,1,L

0	474	590
2	122	121
3	220	-245
4	83	-99
5	117	-141
6	21	-34
7	32	-40
8	75	83
9	27	17
10	24	-5

2,2,L

0	130	156
1	129	-121
2	377	-350
3	228	235
4	25	36
5	66	-69
6	35	-35
7	34	-34
8	87	85
9	0	0
10	7	10

2,3,L

0	450	-530
1	43	-36
2	45	41
3	37	-47
4	151	-150
5	50	-51
6	26	29
7	57	50
8	45	46
9	33	21
10	35	31

2,4,L

0	1170	-1397
1	237	240
2	261	239
3	86	-102
4	120	120
5	44	-49
6	44	30
7	44	46
8	33	30
9	3	0
10	64	54

2,5,L

0	1220	-1370
1	33	-33
2	34	-33
3	547	514
4	96	-92
5	52	-42
6	74	-72
7	0	-0
8	0	-16
9	0	3

2,5,L

10	79	71

2,6,L

0	7	-30
1	236	223
2	79	-71
3	63	-57
4	0	9
5	196	-174
6	14	-22
7	75	72
8	43	-30
9	33	30
10	0	2

2,7,L

0	44	-16
1	10	-2
2	289	277
3	96	-85
4	24	17
5	122	100
6	28	3
7	39	26
8	0	-14
9	2	0

2,8,L

0	346	330
1	249	-240
2	546	509
3	0	-4
4	6	5
5	140	-129
6	101	-90
7	81	77
8	0	-17
9	0	1

2,9,L

0	134	-129
1	66	-56
2	1899	1856
3	97	92
4	22	1
5	156	136
6	106	90
7	0	21
8	10	-13
9	43	-40

2,10,L

0	15	-26
1	27	12
2	943	919
3	91	-86
4	66	56
5	137	-129
6	67	-72
7	53	59
8	53	-35
9	0	-14

2,11,L

0	205	-197
1	165	172
2	375	373
3	122	-117
4	60	-59
5	39	-30
6	121	117
7	66	49
8	13	-6
9	10	0

2,12,L

0	492	485
1	20	11
2	97	-100
3	71	53
4	43	-30
5	93	-95
6	0	-22
7	33	35
8	4	-9
9	61	-52

2,13,L

0	233	-219
1	13	0
2	197	-189
3	290	-295
4	135	-133
5	119	119
6	26	23
7	0	-5
8	27	0
9	17	-7

2,14,L

0	156	162
1	61	55
2	46	52
3	151	157
4	211	-215
5	35	-27
6	44	56
7	20	-21
8	53	-42
9	42	-21

2,15,L

0	75	-70
1	25	20
2	62	-53
3	197	-200
4	227	-233
5	90	84
6	0	-7
7	32	15
8	22	10

2,16,L

0	0	4
1	70	-59
2	27	-27
3	60	70
4	67	-61
5	74	71
6	26	-21
7	41	33
8	42	29

2,17,L

0	159	151
1	39	-24
2	64	-72
3	205	-216
4	112	-125
5	2	3
6	47	44
7	44	49
8	27	-9

2,18,L

0	244	-252
1	0	-1
2	73	-70
3	153	163
4	32	3
5	37	46
6	46	37
7	0	1
8	0	-5

2,19,L

0	58	64
1	62	-59
2	42	-34
3	120	-130
4	41	46
5	20	22
6	22	3
7	20	5
8	0	-3

2,20,L

0	114	117
1	73	-89
2	50	-49
3	5	16
4	33	26
5	0	0
6	0	11
7	4	-12

2,21,L

0	30	-19
1	16	-24
2	10	-15
3	77	74
4	0	2
5	0	0
6	27	22
7	6	-10

2,22,L

0	32	39
1	41	-36
2	26	20
3	44	-54
4	20	35
5	51	-40
6	15	-12
7	4	-5

2,23,L

0	43	44
1	73	77
2	55	54
3	10	40
4	0	-8
5	15	2
6	0	-12
7	20	-14

2,24,L

1	37	33
2	38	45
3	28	24
4	28	22
5	36	-19
6	54	-47

2,25,L

0	23	-22
1	92	101
2	0	-12
3	22	16
4	5	7
5	5	16
6	20	3

2,26,L

0	0	4
1	4	7
2	30	-28
3	26	14
4	72	74
5	13	0

2,27,L

0	33	-36
1	0	-11
2	31	-14
3	39	31
4	0	0
5	12	-12

2,28,L

0	22	6
1	20	-11
2	10	-17
3	0	7
4	21	7

2,29,L

0	24	-22
1	0	-11
2	20	-20
3	45	-38
4	6	5

2,30,L

0	0	19
1	25	-6
2	1	0
3	24	-18

2,31,L

0	0	-3
1	47	-43
2	31	24

2,32,L

0	25	12
1	20	24

3,0,L

0	644	-724
2	53	-53
4	363	402
6	37	51
8	24	-2

3,1,L

0	129	-137
1	120	143
2	76	-74
3	134	122
4	92	-90
5	27	-0
6	30	-39
7	0	3
8	36	26
9	37	30

3,2,L

0	240	-293
1	121	115
2	100	170
3	175	163
4	46	-43
5	39	31
6	0	-9
7	31	-25
8	14	11
9	11	11

3,3,L

0	76	-73
1	126	-110
2	72	-60
3	21	-24
4	257	-246
5	25	29
6	91	-102
7	55	-61
8	62	56
9	0	1

3,4,L

0	125	120
1	0	10
2	151	-144
3	123	-117
4	125	-99
5	00	-04
6	0	-13
7	125	117
8	35	-23
9	52	-42

3,5,L

0	272	320
1	42	-34
2	207	191
3	42	46
4	155	-135
5	0	15
6	136	-135
7	34	-36
8	3	-13
9	40	-40

3,6,L

0	289	309
1	112	100
2	54	-59
3	193	-167
4	42	29
5	139	-120
6	0	10
7	90	91
8	37	-20
9	0	10

3,7,L

0	447	470
1	564	523
2	02	00
3	105	-161
4	4	11
5	29	-20
6	00	-04
7	75	-63
8	37	24
9	49	39

3,8,L

0	240	239
1	502	-467
2	30	25
3	0	3
4	139	-132
5	50	-56
6	105	95
7	29	35
8	22	15
9	53	44

3,9,L

0	192	-102
1	450	-440
2	0	3
3	19	-10
4	152	135
5	43	33
6	67	-64
7	40	34
8	52	35
9	55	-30

3,10,L

0	100	170
1	515	-501
2	102	-99
3	20	24
4	112	-114
5	0	-13
6	12	19
7	31	-13
8	0	0

3,11,L

0	140	-140
1	32	-35
2	45	36
3	3	-7
4	146	137
5	139	127
6	26	-20
7	0	-13
8	31	16

3,12,L

0	303	291
1	116	135
2	100	-97
3	77	74
4	200	-196

3,12,L

5	34	-41
6	7	3
7	28	21
8	0	6

3,13,L

0	32	-42
1	91	-81
2	72	-63
3	212	202
4	248	226
5	52	52
6	35	38
7	28	14
8	13	1

3,14,L

0	183	-183
1	67	-68
2	94	-98
3	421	407
4	137	-136
5	62	68
6	50	38
7	24	-24
8	20	19

3,15,L

0	0	4
1	19	-7
2	86	-89
3	256	262
4	103	89
5	0	-5
6	24	-16
7	20	1
8	0	7

3,16,L

0	288	-282
1	78	-76
2	50	48
3	193	185
4	17	10
5	0	-3
6	29	-19
7	0	-9
8	29	18

3,17,L

0	100	-96
1	77	77
2	97	-95
3	29	-35
4	95	-93
5	0	1
6	40	-31
7	0	2

3,18,L

0	99	104
1	42	-40
2	26	29
3	21	-27
4	22	0
5	55	-57
6	0	12
7	22	-5

3,19,L

0	111	-125
1	90	-96
2	53	-60
3	14	43
4	23	22
5	91	-94
6	0	-5
7	0	-11

3,20,L

0	65	64
1	30	-19
2	84	87
3	54	-40
4	5	-4
5	109	-113
6	0	13
7	26	0

3,21,L

0	83	85
1	10	9
2	0	-15
3	0	11
4	0	-5
5	40	-47
6	0	3

3,22,L

0	80	-89
1	10	-22
2	17	12
3	0	-2
4	0	10
5	60	-50
6	4	1

3,23,L

0	135	-139
1	15	-6
2	0	-10
3	22	19
4	2	-4
5	4	-13
6	0	15

3,24,L

0	61	-61
1	15	5
2	15	22
3	26	-13
4	5	-8
5	0	2

3,25,L

0	30	-29
1	38	42
2	0	-4
3	6	11
4	0	-12
5	40	17

3,26,L

0	12	-3
1	0	27
2	49	-39
3	17	-8
4	0	-8
5	0	15

3,27,L

0	21	16
1	0	8
2	81	77
3	0	12
4	0	13

3,28,L

0	0	-4
1	5	16
2	0	11
3	16	10
4	22	0

3,29,L

0	22	9
1	19	-3
2	52	54
3	13	3

3,30,L

0	8	8
1	22	12
2	45	31

3,31,L

0	14	-8
1	0	-11

3,32,L

0	72	74

4,0,L

0	165	161
2	33	-20
4	29	-27
6	28	39
8	60	-60

4,1,L

0	124	139
1	79	102
2	51	-64
3	89	-95
4	27	-34
5	26	21
6	0	14
7	101	97
8	5	-8

4,2,L

0	303	-312
1	59	-70
2	329	321
3	65	-56
4	76	-72
5	62	48
6	34	35
7	0	-15
8	44	-45

4,3,L

1	0	27
2	149	-141
3	85	76
4	71	-73
5	80	-63
6	0	-14
7	85	81
8	14	21

4,4,L

0	272	-331
1	18	-13
2	240	236
3	80	-81
4	16	-17
5	210	180
6	39	22
7	1	-8
8	42	33

4,5,L

0	179	177
1	30	35
2	190	-175
3	90	-92
4	34	-27
5	0	-6
6	2	12
7	47	49
8	0	-2

4,6,L

0	260	-249
1	65	-56
2	53	40
3	6	-5
4	42	31
5	129	129
6	66	60
7	32	5
8	42	-30

4,7,L

0	295	300
1	9	20
2	34	-20
3	25	16
4	10	-24
5	132	-125
6	16	-20
7	37	-34
8	0	-10

4,8,L

0	210	206
1	93	-84
2	167	-157
3	114	-97
4	16	-30
5	102	85
6	19	9
7	20	-23
8	31	-12

4,9,L

0	277	272
1	2	13
2	70	70
3	39	-45
4	11	-16
5	184	-150
6	19	24
7	50	-49
8	27	-4

4,10,L

0	5	0
1	172	164
2	9	-20
3	84	-80
4	13	2
5	99	89
6	25	-26
7	20	-32
8	3	12

4,11,L

0	50	-30
1	7	-20
2	60	62
3	40	36
4	0	20
5	23	19
6	15	-15
7	59	-42

4,12,L

0	35	26
1	235	230
2	25	-0
3	49	45
4	32	-29
5	64	-47
6	0	13
7	32	-29

4,13,L

0	236	-229
1	125	125
2	276	-264
3	63	61
4	21	10
5	57	46
6	12	-17
7	19	-6

4,14,L

0	209	213
1	186	-196
2	370	-369
3	27	-32
4	36	49
5	25	10
6	6	-3
7	34	-20

4,15,L

0	84	80
1	30	-37
2	126	-123
3	67	65
4	26	-3
5	53	30
6	0	-12
7	0	-9

4,16,L

0	341	-350
1	51	-50
2	30	-32
3	0	-0
4	51	47
5	0	-1
6	44	26
7	24	-23

4,17,L

0	144	140
1	3	-7
2	89	86
3	45	-33
4	95	91
5	0	-3
6	45	-23

4,18,L

0	69	-77
1	62	-62
2	26	20
3	27	-27
4	140	140
5	0	-10
6	0	10

4,19,L

0	93	-89
1	31	20
2	53	-62
3	0	-1
4	146	150
5	27	-10
6	13	0

4,20,L

0	57	-50
1	32	-42
2	2	15
3	25	11
4	119	126
5	0	-17
6	26	14

4,21,L

0	39	49
1	24	-33
2	0	-5
3	26	-9
4	53	41
5	22	-29

4,22,L

0	0	-12
1	16	-22
2	34	36
3	55	45
4	2	-17
5	6	-9

4,23,L

0	15	20
1	0	10
2	21	3
3	60	-44
4	20	-30
5	20	-24

4,24,L

0	48	50
1	35	16
2	4	0
3	23	1
4	21	-9

4,25,L

0	0	-1
1	23	31
2	10	20
3	0	3
4	20	-6

4,26,L

0	34	31
1	22	-1
2	11	3
3	0	0

4,27,L

0	0	23
1	36	27
2	3	-9
3	12	-14

4,28,L

0	31	11
1	84	-90
2	0	-12

4,29,L

0	42	37
1	27	-20
2	0	13

4,30,L

0	27	-20
1	0	-4

4,31,L

0	0	20

5,0,L

0	197	215
2	90	117
4	25	-25
6	53	-60

5,1,L

0	136	-155
1	131	-135
2	100	-119
3	61	80
4	49	33
5	0	1
6	12	14
7	53	53

5,2,L

0	84	82
1	69	79
2	38	44
3	121	130
4	5	-2
5	21	24
6	85	-72
7	25	-19

5,3,L

0	219	-235
1	131	-110
2	124	-121
3	63	60
4	21	-23
5	32	17
6	96	76
7	33	29

5,4,L

0	2	7
1	69	-71
2	35	42
3	33	27
4	73	-69
5	44	31
6	111	-84
7	25	11

5,5,L

0	37	45
1	10	10
2	9	0
3	60	-56
4	66	-70
5	0	-0
6	100	77
7	2	-1

5,6,L

0	72	66
1	102	-100
2	85	-91
3	63	-59
4	20	5
5	31	15
6	0	-3
7	7	17

5,7,L

0	71	67
1	0	1
2	30	-23
3	42	40
4	42	25
5	90	-77
6	20	12
7	0	12

5,8,L

0	42	37
1	177	-179
2	30	20
3	0	10
4	66	60
5	1	7
6	52	30
7	34	-22

5,9,L

0	59	66
1	53	49
2	165	-161
3	37	34
4	71	-70
5	22	-3
6	34	30
7	32	-19

5,10,L

0	46	-37
1	36	30
2	27	19
3	41	39
4	43	30
5	5	-13
6	0	22
7	21	1

5,11,L

0	24	31
1	327	-327
2	32	-24
3	2	9
4	21	-15
5	30	29
6	0	2
7	6	10

5,12,L

0	61	-55
1	252	254
2	31	-32
3	17	13
4	0	12
5	10	-1
6	30	-23

5,13,L

0	172	164
1	0	-4
2	26	29
3	0	16
4	7	-3
5	0	-20
6	36	-30

5,14,L

0	59	-71
1	101	111
2	74	63
3	0	-1
4	34	20
5	43	-41
6	4	-3

5,15,L

0	87	86
1	0	-10
2	77	74
3	60	52
4	31	-19
5	31	1
6	0	-3

5,16,L

0	30	44
1	49	40
2	37	52
3	35	33
4	4	17
5	29	-19

5,16,L

6	0	1

5,17,L

0	64	-61
1	54	-72
2	90	87
3	25	-21
4	50	42
5	0	0

5,18,L

0	24	-7
1	47	44
2	36	46
3	134	-124
4	56	-36
5	28	-22

5,19,L

0	27	24
1	72	68
2	21	-6
3	146	-146
4	3	6
5	8	14

5,20,L

0	35	-27
1	61	-52
2	34	-35
3	50	-60
4	0	-17
5	0	4

5,21,L

0	20	-21
1	27	19
2	28	-22
3	27	-21
4	0	-7

5,22,L

0	70	67
1	29	-26
2	62	51
3	12	17
4	37	-29

5,23,L

0	0	12
1	10	21
2	77	-65
3	10	-16
4	0	-10

5,24,L

0	57	58
1	19	19
2	17	9
3	15	-8

5,25,L

0	0	-4
1	43	-36
2	22	-20
3	37	-27

5,26,L

0	43	40
1	30	25
2	0	-19

5,27,L

0	99	105
1	0	4
2	42	-25

5,28,L

0	0	4
1	10	6

5,29,L

0	46	47

6,0,L

0	237	263
2	66	-58
4	29	-17
6	22	7

6,1,L

0	36	43
1	62	69
2	25	-34
3	0	-16
4	5	-7
5	61	42
6	0	3

6,2,L

0	242	260
1	44	-43
2	49	-52
3	33	35
4	11	10
5	0	6
6	9	-13

6,3,L

0	0	9
1	77	74
2	164	-177
3	22	25
4	0	3
5	31	30
6	22	15

6,4,L

0	96	-101
1	15	12
2	32	26
3	9	13
4	44	28
5	46	-33
6	20	4

6,5,L

0	198	-199
1	24	-10
2	55	-63
3	47	40
4	73	60
5	61	44
6	26	-15

6,6,L

0	53	-56
1	37	-43
2	189	-183
3	24	11
4	31	31
5	23	-2
6	0	0

6,7,L

0	16	-11
1	71	-70
2	80	86
3	17	-5
4	90	89
5	0	-6
6	11	7

6,8,L

0	202	-211
1	63	-64
2	154	-145
3	15	2
4	22	40
5	3	-8
6	11	-4

6,9,L

0	280	311
1	153	-163
2	20	33
3	35	31
4	11	15
5	40	-42
6	20	-15

6,10,L

0	121	-129
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2	32	16
3	0	5
4	0	-7
5	55	-44
6	0	-8

6,11,L

0	140	-151
1	40	47
2	24	31
3	44	-27
4	17	-5
5	30	-21

6,12,L

0	189	203
1	40	36
2	21	-16
3	5	3
4	36	20
5	30	17

6,13,L

0	164	-169

6,13,L

1	44	42
2	0	17
3	20	35
4	24	-2
5	45	-26

6,14,L

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1	95	101
2	3	9
3	0	-4
4	0	3
5	0	-2

6,15,L

0	33	19
1	28	-22
2	37	-41
3	0	-1
4	5	-6
5	35	-23

6,16,L

0	115	116
1	24	-12
2	26	32
3	44	-38
4	24	-8
5	0	1

6,17,L

0	53	-60
1	46	42
2	38	34
3	46	24
4	16	-8

6,18,L

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1	39	36
2	93	91
3	71	-52
4	3	0

6,19,L

0	34	24
1	78	82
2	62	61
3	39	36
4	7	0

6,20,L

0	0	10
1	0	10
2	45	-39
3	5	15

6,21,L

0	0	11
1	0	21
2	7	-1
3	35	17

6,22,L

0	0	-6
1	6	22
2	45	-38
3	19	18

6,23,L

0	21	20
1	64	-63
2	12	14

6,24,L

0	25	9
1	34	17
2	13	2

6,25,L

0	20	-26
1	0	-4

6,26,L

0	2	-1
1	30	-20

6,27,L

0	0	-12

7,0,L

0	0	10
2	32	-46
4	53	50

7,1,L

0	40	-51
1	13	-13
2	0	-9
3	12	-1
4	0	16
5	2	3

7,2,L

0	0	6
1	60	56
2	25	-4
3	175	154
4	11	20
5	0	12

7,3,L

0	56	-55
1	65	-77
2	42	44
3	34	-40
4	17	5
5	19	21

7,4,L

0	35	41
1	196	192
2	81	-71
3	42	60
4	0	0
5	0	0

7,5,L

0	84	-89
1	56	-63
2	110	102
3	39	-36
4	27	23
5	0	-1

7,6,L

0	115	116
1	50	-54
2	26	20
3	0	0
4	0	-9
5	20	-6

7,7,L

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1	200	220
2	37	20
3	72	-60
4	33	23
5	0	-10

7,8,L

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1	124	-132
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3	0	-5
4	30	18
5	34	-17

7,9,L

0	14	9
1	11	25
2	45	35
3	19	-21
4	13	17
5	20	6

7,10,L

0	80	-80
1	70	-66
2	19	-16
3	1	-20
4	3	-10

7,11,L

0	17	-24
1	64	55
2	17	-10
3	13	-3
4	24	-17

7,12,L

0	46	-49
1	80	-76
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3	60	-63
4	1	1

7,13,L

0	26	-7
1	59	65
2	57	-49
3	24	-14
4	59	-39

7,14,L

1	41	38
2	25	18
3	9	-16
4	47	25

7,15,L

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1	15	15
2	18	-22
3	29	-14

7,16,L

0	24	-35
1	43	32
2	48	47
3	23	12

7,17,L

0	29	-22
1	31	-28
2	42	24
3	0	-12

7,18,L

0	25	-21
1	21	18
2	45	-31
3	7	-1

7,19,L

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2	47	37

7,20,L

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7,21,L

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1	0	14
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7,22,L

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1	0	-6

7,23,L

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1	44	-42

7,24,L

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8,0,L

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2	113	-116
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8,1,L

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1	62	56
2	99	-100
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4	39	-22

8,2,L

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2	33	47
3	18	-8
4	41	-41

8,3,L

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1	25	-23
2	74	-78
3	23	8
4	50	-33

8,4,L

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1	60	59
2	58	62
3	24	17
4	36	-17

8,5,L

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1	23	-8
2	5	1
3	0	-23
4	14	2

8,6,L

0	23	-38
1	55	50
2	37	37
3	9	2

8,7,L

0	92	97
1	9	-18
2	26	-4
3	6	16

8,8,L

0	91	-91
1	24	19
2	43	46
3	0	-7

8,9,L

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3	27	2

8,10,L

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2	20	11
3	0	-11

8,11,L

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2	31	27
3	0	12

8,12,L

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1	38	48
2	14	0
3	18	1

8,13,L

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1	49	41
2	0	-4

8,14,L

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2	31	-26

8,15,L

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1	36	-27
2	31	-43

8,16,L

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1	43	-26
2	12	6

8,17,L

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1	46	-36

8,18,L

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1	39	-27

8,19,L

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1	23	-19

8,20,L

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8,21,L

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9,0,L

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9,1,L

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2	24	2

9,2,L

0	95	-89
1	186	184
2	3	-14

9,3,L

1	75	-74
2	38	34

9,4,L

0	29	-25
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2	42	34

9,5,L

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1	28	13
2	38	19

9,6,L

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1	0	36
2	48	19

9,7,L

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1	6	-7
2	0	8

9,8,L

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1	11	34
2	0	1

9,9,L

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1	17	10
2	10	5

9,10,L

0	23	-23
1	0	12

9,11,L

0	65	-61
1	0	-19

9,12,L

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1	0	-16

9,13,L

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1	13	12

9,14,L

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1	0	-18

9,15,L

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9,16,L

0	25	26

9,17,L

0	3	-5

10,0,L

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10,2,L

0	27	5

10,3,L

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10,4,L

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10,5,L

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10,6,L

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10,7,L

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10,8,L

0	10	6

10,9,L

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10,10,L

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END

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